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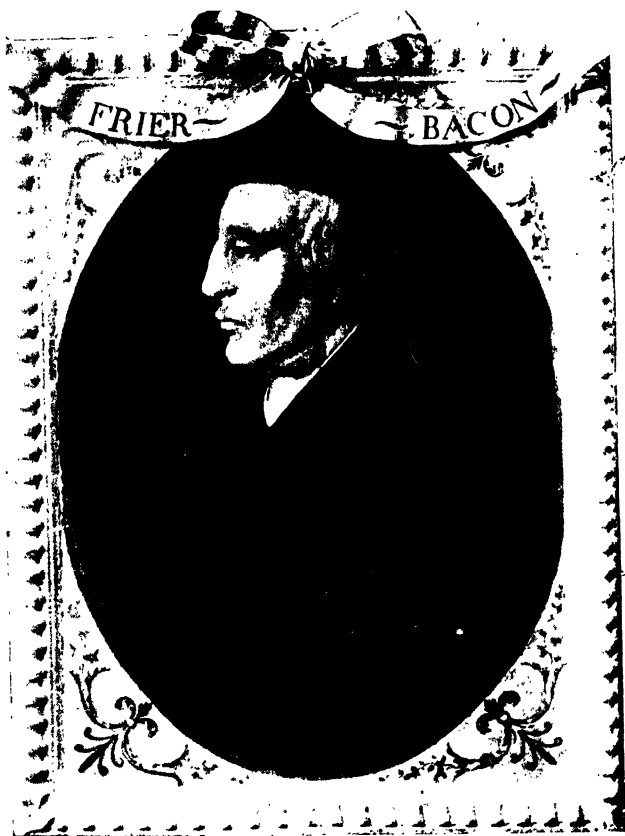












ROGER BACON.

From a painting in the possession of Lord Sackville at Knole.

# HISTORY OF CHEMISTRY

BY

SIR EDWARD THORPE,  
C.B., LL.D., F.R.S.

AUTHOR OF "ESSAYS IN HISTORICAL CHEMISTRY," "HUMPHRY DAVY :  
POET AND PHILOSOPHER," "JOSEPH PRIESTLEY," ETC., ETC.

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## · CHAPTER I.

### THE CHEMISTRY OF THE ANCIENTS

CHEMISTRY, as an art, was practised thousands of years before the Christian era; as a science, it dates no further back than the middle of the seventeenth century. The monumental records of Egypt and the accounts left us by Herodotus and other writers show that the ancient Egyptians, among the earliest nations of whom we have any records, had a considerable knowledge of processes essentially chemical in their nature. Their priests were adepts in certain chemical arts, and chemical laboratories were occasionally attached to their temples, as at Thebes, Memphis, and Heliopolis. It is to be supposed, too, that in a cultured class, as the priesthood undoubtedly was, there would be now and again curious and ingenious persons who would speculate on the nature and causes of the phenomena which they observed. But there is no certain evidence that the Egyptians ever pursued chemistry in the spirit of science, or even in the manner in which they and the Chaldeans followed, for example, astronomy or mathematics. The operations of chemistry as performed by them were of the nature of manufacturing processes, empirical in character and utilitarian in result. It was comparatively late in the world's history that men were found willing to occupy themselves in chemical pursuits in order to gain an insight.

into the nature of chemical change, and to learn the causes and conditions of its action.

Although we have cited the ancient Egyptians as practising the chemical arts, there is no proof that these arts actually originated with them. China, India, Chaldæa have each in turn been regarded as the birth-place of the various technical processes from which chemistry may be said to have taken its rise. Nevertheless, it is mainly from Egyptian records, or from writings avowedly based on information from Egyptian sources, that such knowledge as we possess of the earliest chemical processes is derived. It is significant that the word "chemistry" has its origin in *chêmi*, "the black land," the ancient name for Egypt. The art itself was constantly spoken of as the "Egyptian art."

"The word *chemistry*," says Boerhaave, in the Prolegomena of his *New Method of Chemistry* (Shaw and Chambers's translation, London, 1727),

in *Greek* should be wrote *χημα*, and in *Latin* and *English* *chemia* and *chemistry*; not as usual, *chymia* and *chymistry*.

The first author in whom the word is found is *Plutarch*, who lived under the Emperors *Domitian*, *Nerva*, and *Trajan*. That philosopher, in his treatise of *Isis* and *Osiris*, takes occasion to observe that *Egypt*, in the sacred dialect of the country, was called by the same name as the black of the eye—viz., *χημα*—by which he seems to intimate that the word *chemia* in the *Egyptian* language signified black, and that the country, *Egypt*, might take its denomination from the blackness of the soil.

But [continues Boerhaave] the etymology and grammatical signification of the name is not so easily dispatched. The critics and antiquaries, among whom it has been a great subject of inquiry, will not let it pass without some further disquisition. Instead of *black*, some will have it originally denote *secret*, or *occult*; and

hence derive it from the *Hebrew chaman*, or *haman*—a *mystery*, whose radix is *cham*. And, accordingly, *Plutarch* observes that *Egypt*, in the same sacred dialect, is sometimes wrote in *Greek* *χαμα*—*chamia*; whence the word is easily deduced further from *Cham*, eldest son of *Noah*, by whom *Egypt* was first peopled after the deluge, and from whom, in the Scripture style, it is called the *land of Cham*, or *Chem*. Now, that *chaman*, or *haman*, properly signifies *secret* appears from the same *Plutarch*, who, mentioning an ancient author named *Menethes Sibonita*, who had asserted that *Ammon* and *Hammon* were used to denote the god of *Egypt*, *Plutarch* takes this occasion to observe that in the *Egyptian* language anything secret or occult was called by the same name, *αμμον*—*Hammon*..... Lastly, the learned *Bochart*, keeping to the same sense of the word, chooses to derive it from the *Arabic chema*, or *kema*—to *hide*; adding that there is an *Arabic* book of secrets called by the same name *Kemi*.

From the whole of which *Boerhaave* gathers that chemistry was thus originally denominated because it was considered of old as “not fit to be divulged to the populace, but treasured up as a religious *secret*.”

If we are to credit *Zozimus* the *Panopolite*, who is said to have lived about the beginning of the fifth century, there were sound reasons for thus treasuring up chemistry as a religious secret, since, as it sprang from the *pretium amoris*, its origin was not too reputable. “What the divine writings relate is that the angels, enflamed with the desire of women, instructed ’em in all the works and mysteries of nature. For which indiscretion they were excluded heaven, as having taught men things unfit for ’em to know.” And *Scaliger* asserts that “*Hermes* testifies as much; and all our learning, both open and occult, confirms the account.” But who *Hermes* was, adds that author<sup>2</sup>, is

hard to say, for none of his writings has survived to our age, "that lately published in Italy under the name of *Hermes Trismegistus* being a manifest forgery."

This legend of the "feministic" origin of chemistry is in reality much older than the fifth century of our era, and is but a variant of that which, according to Jewish writers, led to the expulsion of man from Paradise. A similar myth was current among the Phœnicians, Persians, Greeks, and Magi. We trace it in the legend of Sibylla, who demanded, as the price of her favour to Phœbus, not only length of years, but a knowledge of the divine *arcanum*. Some of the ecclesiastics who elaborated these myths are particular in their accounts of the mysteries thus imparted. They included the use of charms, a knowledge of gold and silver and precious stones, the art of dyeing, of painting the eyebrows, etc.—the kind of *arcana*, in fact, which women in all ages were presumably most keen to know. It is, however, significant that in all allusions to *chemia*, even after the translation of the seat of the Roman Empire to Constantinople, it is implied that a knowledge of it was a sacred mystery, to be known only to the priesthood, and jealously guarded by them. It was characteristic of writers who had affixed an eternal stigma on Eve to make the sex in general answerable for an illicit knowledge of "things unfit for men to know."

For, in reality, chemistry originated with men, and it was not so much in the love of women as of wine that it took its rise.

The manufacture of *alcohol* by processes of fermentation is probably the oldest of the chemical arts. The word *wine* means, in fact, a *product of fermentation*. Mosaic history relates that Noah, soon after he got to

dry land, "planted a vineyard and drank of the wine," with results that would appear to show that the potency of wine was not unfamiliar to him. Diodorus Siculus, who studied Egyptian antiquities when Egypt was a Roman province, states that the ancient Egyptians ascribed the origin of wine to Osiris. It was a sacrificial offering even in the earliest times, as was bread. Wine seems to have been prepared by the Chinese as far back as the time of the Emperor Yü, *circa* 2220 B.C. Beer was manufactured in Egypt in the time of Senwosret III. (Sesostris) B.C. 1880.

The Egyptians were skilled in dyeing and in the manufacture of leather, and in the production and working of metals and alloys. They were familiar with the methods of tempering iron. They made glass, artificial gems, and enamels. The oldest known enamel was found as an amulet on the Egyptian Queen Aahotep (1700 B.C.), and glass beads were made before the time of Thutmosis III. (1475 B.C.). The Jews knew of gold, silver, copper, iron, lead, and tin. Indeed, it is through them and the Phœnicians, who were among the earliest of traders, that Europe was gradually made acquainted with many technical products of Eastern origin.

The beginnings of the art of extracting and working of metals are lost in the mists of antiquity; the chemistry of metals, indeed, has been said to be almost coeval with mankind. Diodorus Siculus found traditions in Egypt as to the first inventor of metallurgical processes identical with that of the son of Lamech and Zillah, Tubal-cain or Tuval-cain of the Hebrews—the Vulcan of the Romans.

Gold was undoubtedly one of the earliest metals to be made use of by men, as it probably was one of the

first to be discovered. It occurs free in nature, and is met with in many rocks and in the sands of rivers. Its colour, lustre, and density would early attract attention to it; and its malleability and ductility and the ease with which it could be fashioned, together with its unalterability, would render it valuable. Ethiopian and Nubian gold were known from the earliest times, and quartz crushing and gold washing were practised by the Egyptians. Representations of these processes have been found on Egyptian tombs dating from 2500 B.C. Gold-wire was used by the Egyptians for embroidery, and they practised plating, gilding, and inlaying as far back as 2000 B.C.

*Silver* also was employed by them, and appears, like gold, to have been coined into money. It was originally known as "white gold." Some of the oldest coins in existence are alloys of silver and gold, obtained probably by the fusion of naturally occurring argentiferous gold, such as the pale gold of the Pactolus. Such an alloy was termed *electrum*, from its resemblance in colour to amber.

*Copper* is also found to a limited extent in the metallic state, but probably the greater part of that used by the ancients was obtained from its ores, which are comparatively abundant and readily smelted. It was also used for coinage by the Egyptians, and was fashioned by them into a variety of utensils and implements. The older writers drew no clear distinction between copper, bronze, and brass, and the terms designating them—*æs* and χαλκός—are frequently employed, as by Pliny, indiscriminately. The statement in Deut. viii. 9—"Out of whose hills thou mayest dig brass"—obviously cannot mean an alloy of copper and zinc, since this does not occur naturally.

Pure copper is too soft a metal to be used for swords and cutting instruments, but copper ores frequently contain associated metals, as, for example, tin, which would confer upon the copper the necessary hardness to enable it to be fashioned into weapons. Such copper would be of the character of bronze, and it was known to the early workers that the nature of the metal was greatly modified by the selection of ores from particular localities. It was comparatively late in the metallurgical history of copper that bronze was produced by knowingly adding tin to the metal.

Copper was largely used by the Romans, who obtained it from Cyprus; it was known to them as *æs Cyprium*, and eventually *Cuprum*, whence we obtain the chemical symbol Cu. What the Romans called *æs* was found also at Chalkis, in Eubœa, whence χαλκός, the Greek word for copper.

*Aurichalcum*, or golden copper—that is, brass—was well known to the early workers in copper, and was made in Pliny's time by heating together copper, cadmia (calamine), and charcoal.

Bell metal was employed by the Assyrians, and bronze was cast by the Egyptians for the manufacture of mirrors, vases, shields, etc., as far back as 2000 B.C. Statuary bronze, largely used by the Romans, usually contained more or less lead.

*Tin*, which was also known to the early Egyptians, would appear to have been first obtained from the East Indies, and to have been known under the Sanskrit name of *Kastira* (*Kâs*, to shine), whence we have the Arabic word for tin, *Kâsdir*, and the Greek κασσιτερος, used by Homer and Hesiod. Tin ores are found in Britain (Cornwall), and were brought thence by the Phœnicians. The group of islands, including the Scilly Islands and



the larger island to the east (Britain), was known to the Romans as the *Insulæ Cassiterides*.

Pliny states that the tin is found in grains in alluvial soil, from which it is obtained by washing; but he gives no description of the method of smelting. The Latin word for tin was *stannum*; it was also known as *plumbum album*, in contradistinction to lead, which was called *plumbum nigrum*. Tin was used by the Romans for covering the inside of copper vessels, and was also occasionally employed in the construction of mirrors.

*Lead* was well known to the Egyptians. In Pliny's time it was mainly procured from Spain and from Britain (Derbyshire). Leaden pipes were used by the Romans for the conveyance of water, and sheet lead was employed by them for roofing purposes. The Romans were also aware of alloys of lead and tin. *Argentarium* was composed of equal parts of lead and tin; *tertiarium*, used as a solder, consisted of two parts of lead and one part of tin.

*Iron*, although now the most important of the common metals, was not in general use until long after the discovery of gold, silver, and copper. This was probably due to the fact that, although its ores are relatively abundant and widely distributed, its extraction as a metal demanded greater skill and more appliances than were possessed by the earlier races. Metallic iron was, however, well known to the Egyptians, who employed it in the manufacture of swords, knives, axes, and stone-chisels, both as malleable iron and as steel. Steel was also known to the Chinese as far back as 2220 B.C., and they were acquainted with the methods of tempering it. The good quality of Chinese steel caused it to be highly prized by Western nations. The earliest people to smelt iron are supposed to have been the

Chalybes, a nation inhabiting the neighbourhood of the Black Sea; it is from them that the ancient name for steel—*chalybs*—is derived, and also our word “chalybeate.” •

*Mercury* has long been known, but there is no evidence that the ancient Egyptians were aware of its existence, or it would probably have been mentioned by Herodotus. It was familiar to Aristotle, and its mode of manufacture from cinnabar is described by Theophrastus (320 B.C.), who terms it “liquid silver.” Processes of amalgamation were known to Pliny, who notes the readiness with which mercury dissolves gold. Pliny appears to distinguish the native metal found in Spain, which he terms *argentum vivum* (quicksilver), from that obtained by sublimation or distillation from cinnabar, which he calls *hydrargyrum*, from which we get the chemical symbol for mercury Hg.

A considerable number of metallic compounds were known to the ancients, and were employed by them as medicines and as pigments. The oxides of copper, known as *flos æris*, and *scoria æris*, obtained by heating copper bars to redness and exposing them to air, were used as escharotics. Verdigris, or *æруго*, was made by the same methods as now. Blue vitriol, or *chalcantum*, is described by Pliny, who says that the blue transparent crystals are formed on strings suspended in its solution.

*Chrysocolla*, malachite, or copper carbonate, was used as a green pigment. • The blue *κύανος* of the Greeks, or *cæruleum* of the Romans, was obtained by fritting together alkali, sand, and oxide of copper. *Botryitis*, *placitis*, *onychitis*, *ostracitis*, were varieties of *cadmia* or oxide of zinc, obtained by calcining calamine, and were used in the treatment of ulcers, etc.

*Molybdena*, which was the Latin name for litharge, was employed externally as an astringent and in the manufacture of plaster. The lead plaster employed by Roman surgeons was practically identical in character and mode of preparation with that in use to-day. *Cerussa*, or white lead, was made as now by exposing sheets of lead to the fumes of vinegar. It was used in medicine, as a pigment, and in the preparation of cosmetics. *Cerussa usta* was probably red lead. Its present name of *minium* was originally applied to cinnabar, the red sulphide of mercury, which was frequently adulterated with red lead.

*Cinnabar*, formerly obtained from Africa, and, by the Romans, from Spain, was also used externally in medicine, and was a highly prized pigment, whose value was known to the Chinese from very early times. The black sulphide of antimony, the *stimmi* and *stibium* of Dioscorides and Pliny, was employed by women in Asia, Greece, and latterly in Western Europe, and is still so used in the East, for blackening their eyelashes. Preparations of antimony were used in medicine. *Realgar*, the scarlet sulphide of arsenic, the *sandarach* of Aristotle, and the *arrenichon* of Theophrastus, was employed as a pigment, and also in medicine, both internally and externally. The yellow sulphide of arsenic, or *auri pigmentum* (orpiment), was also used for the same purposes.

A variety of yellow and red ochres, in addition to the pigments above mentioned, were used by painters, such as *rubrica*, an iron ochre of a dark red colour, and *sinopis*, or reddle, obtained from Egypt, Lemnos, and the Balcaric Isles. Oxides of manganese were used as brown pigments. The white pigment, *paratonium*, was probably meerschaum. *Melinum* was a variety of

chalk found in Samos. The ancients were well acquainted with indigo and madder, and with the mode of manufacturing lakes, which were employed by Grecian artists •

The famous *purpurisum* was chalk or clay stained by immersion in a solution of Tyrian purple. *Atramentum* was lamp-black : ivory-black was used by Apelles, and was known as *elephantinum*. The ink of the ancients consisted of lamp-black suspended in a solution of gum or glue. The *atramentum indicum*, imported from the East, was identical with China ink.

The ancients were well skilled in the art of dyeing, and even of calico printing. The Tyrians produced their famous purple dye as far back as 1500 B.C. It was obtained from shell-fish, mainly species of *Murex*, inhabiting the Mediterranean. Tyrian purple has been shown to be dibrom-indigo, and to have been produced by the action of air and light upon the juices exuded from the shell-fish. The fine linen of the Old Testament was probably cotton, for the production of which Egypt was long celebrated. That the Egyptians were acquainted with the use of mordants seems evident from the following passage from Pliny, quoted by Thomson :—

There exists in Egypt a wonderful method of dyeing. The white cloth is stained in various places, not with dye stuffs, but with substances which have the property of absorbing colours ; these applications are not visible upon the cloth, but when they are dipped into a hot caldron of the dye they are drawn out an instant after dyed. The remarkable circumstance is that, though there be only one dye in the vat, yet different colours appear upon the cloth ; nor can the colour be afterwards removed.

This passage accurately describes the process of madder dyeing on cotton, whereby a variety of fast colours—reds, browns, and purples—can be obtained from the same vat by the employment of different mordants, such as alumina, oxide of iron, or oxide of tin, etc.

Glass has been known from very early times. Representations of glass-blowing were found on the monuments of Thebes and Beni Hassan, and large quantities of glass were exported to Greece and Rome from Egypt, mainly by Phœnicians. Aristophanes mentions it as *hyalos*, and speaks of it as the beautiful transparent stone used for kindling fire. The Egyptians made use of various metallic oxides in colouring glass. The *hæmatinon* of Pliny was a red glass coloured with cuprous oxide. Cupric oxide was used to colour glass green; and ancient blue glass has been found to contain cobalt. The costly *vasa murrhina* of the Romans, obtained from Egypt, probably consisted of fluorspar, identical with the Blue John of the Derbyshire mines.

Stoneware has been made from time immemorial, and the Chinese have manufactured porcelain from very remote periods. Bricks and tiles were made by the Romans, and mortar and stucco were employed by the ancient Egyptians.

Soap (*sapo*) is mentioned by Pliny, but its detergent properties were apparently unknown to him. It appears to have been first made by the Gauls, who prepared it from the ashes of the beech and the fat of goats, and used it as a pomatum, as did the *jeunesse d'orée* of Rome. Wood ashes, as well as natron, were, however, used by the ancients for their cleansing properties.

Starch, acetic acid, sulphur, alumen or crude sulphate of alumina, beeswax, camphor, bitumen, naphtha, asphalt, nitrum (carbonate of soda), common salt, and lime, were all well known to the Egyptians, and were used by them for many of the purposes in which they are employed to-day.

It will be evident from this brief survey that the ancients possessed a considerable acquaintance with many operations of technical chemistry; but, although they must necessarily have accumulated a large amount of knowledge, very little has come down to us concerning the mode in which their processes were conducted, or as to the precautions they employed to ensure uniform results. Their methods were probably jealously guarded and handed down by successive members of the crafts as precious secrets. The experienced masters of these crafts must have met with many strange and perplexing phenomena in the course of their operations, and a spirit of inquiry must thereby at times have been awakened. But, under the conditions in which their industries were prosecuted, the scientific spirit was not free to develop, for science depends essentially upon free inter-communication of facts and the spread of knowledge of natural phenomena. Moreover, the great intellects of antiquity, for the most part, had little sympathy with the operations of artisans, who, at least among the Greeks and Romans, were, for the most part, slaves. Philosophers taught that industrial work tended to lower the standard of thought. The priests, in most ages, have looked more or less askance at attempts, on the part of the laity, to inquire too closely into the causes of natural phenomena. The investigation of nature in early times was impossible for religious reasons.

There was an outcry in Athens when the thunderbolts of Zeus were ascribed to the collision of clouds. Anaxagoras, Diogenes of Apollonia, Plato, Aristotle, Diagoras, and Protagoras were charged by the priests with blasphemy and driven into exile. Prodikos, who deified the natural forces, as did Empedokles the primal elements, was executed for impiety. Sacerdotalism in Athens had no more sympathy with science than had the Holy Congregation in Italy when it banned the writings of Copernicus, Kepler, and Galileo, and sent Giordano Bruno to the stake. The educated Greeks had no interest in observing or in explaining the phenomena of technical processes. However prone they might be to speculation, they had no inclination to experiment or to engage in the patient accumulation of the knowledge of physical facts. "You Greeks," says Plato in one of his Dialogues, "are ever children, having no knowledge of antiquity, nor antiquity of knowledge!" The influence of a spurious Aristotelianism, which lasted through many centuries and even beyond the time of Boyle, was wholly opposed to the true methods of science, and it was only when philosophy had shaken itself free from scholasticism that chemistry, as a science, was able to develop.

## CHAPTER II.

### THE CHEMICAL PHILOSOPHY OF THE ANCIENTS

SPECULATIONS as to the origin and nature of matter, and as to the conditions and forces which affect it, are to be found, more or less imperfectly developed, in the oldest systems of philosophy of which we have any record. These speculations are not based, in any real sense, upon the systematic observation of natural phenomena. Still, as they appealed to human reason, they must be held to be founded upon experience, or at least not to be consciously inconsistent with it. All the oldest cosmogonies regarded water as the fundamental principle of things: from Okeanos sprang the gods—themselves deified personifications of the “elements” or principles of which the world was made.

In the course of time this doctrine of the origin and essential nature of matter came to be more particularly associated with the name of Thales of Miletus, who lived six centuries before our era, and who, according to Tertullian, is to be regarded as the first of the race of the natural philosophers—that is, the first of those who made it their business to inquire after natural causes and phenomena. Thales is known to have passed some years of his life in Egypt, and to have been instructed in science by the priests of Thebes and Memphis; and it is therefore possible that he may have been influenced



by the Egyptian teaching in the formulation of his cosmological theories.

It is significant of the tenacity with which the mind clings to dogma and reveres authority that the teaching of Thales should have survived through the space of twenty-four centuries. It can be shown to have affected the course of chemical inquiry down to the close of the eighteenth century. It influenced the experimental labours of philosophers so diverse in character as Van Helmont, Boyle, Boerhaave, Priestley, and Lavoisier—all of whom made attempts to prove or disprove its adequacy. Van Helmont, indeed, was one of the most strenuous supporters of the doctrine of Thales, and sought to establish it by observations which, in the absence of all knowledge of the true nature of air and water, seemed at the time irrefutable. Perhaps the one most frequently cited is his observation on the growth of a plant which apparently had no other form of sustenance than water. He describes how he planted a willow weighing 5 lbs. in 200 lbs. of earth previously dried in an oven. The plant was regularly watered, when at the end of five years it was found to weigh 169 lbs. 3oz., whereas the earth, after redrying, had lost only 2 oz. in weight. Hence, 164 lbs. of woody matter, leaves, roots, etc., had been produced seemingly from water alone. More than a century had to elapse before any clue to the true interpretation of Van Helmont's experiment was gained. It was first furnished by the observations of Ingenhousz and Priestley.

Although the idea of a primal "element" or common principle is to be found in every old-world philosophical system, the ancient philosophers were by no means in agreement as to its character. Anaximenes, who

lived *circa* 500 B.C., taught that it was air, Hera-  
kleitos of Ephesus that it was fire, and Pherekides  
that it was earth. The supposition that a single  
primordial principle could be made to account for  
all forms of matter and all the phenomena and  
manifestations of the material world had its difficulties.  
Attempts to group qualities as principles, and to con-  
struct from these principles the universe, were indeed  
made even prior to the age of Thales. It was a com-  
paratively simple evolutionary step to regard these  
principles or "elements" as mutually convertible.  
Anaximenes' theory of the formation of rain was an  
implicit admission of such convertibility. This philo-  
sopher taught that rain came by the condensation of  
clouds, which in their turn were formed by the conden-  
sation of air. Everything comes from air, and everything  
returns to air. That water might be converted by fire  
into air was surmised from the earliest times. Such a  
supposition naturally sprung from the circumstance  
that water was everywhere recognised to disappear or  
to pass into the air under the influence of fire or solar  
heat. The supposition had grown into a fixed belief in  
the Middle Ages. Even Priestley, as late as the end of  
the eighteenth century, imagined for a time that he had  
obtained proof of such a mutual conversion. The possi-  
bility of the transmutation of water into earth was a  
belief current through twenty centuries, and was only  
definitely and finally disproved by Lavoisier in 1770.  
The conception of fire as the primal principle has its  
germ in the fire- or sun-worship of the Chaldeans,  
Scythians, Persians, Parsees, and Hindus; and it is  
not difficult to trace, therefore, how heat came to be  
regarded either as antecedent to, or as associated with,  
the other primal principles. Empedokles, apparently,

was the first whose name has come down to us to reintroduce the definite conception of four primal elements—fire, air, water, and earth. These he regarded as distinct, and incapable of being transmuted, but as forming all varieties of matter by intermixture in various proportions. These principles he deified, Zeus being the personification of the element of fire, Here of air, Nestis of water, and Aidoneus of earth.

The doctrine of the four elements was also adopted by Plato and amplified by Aristotle, with whose name indeed it is commonly associated. Aristotle, the greatest scientific thinker among the Greeks, exercised an authority almost supreme in Europe during nearly twenty centuries. His influence is to be traced throughout the literature of chemistry long after the time of Boyle. It may be detected even now. Probably few who write chemical memoirs to-day, and who follow the time-honoured practice of prefacing their own contributions to knowledge by a statement of what is already known on the subject, are aware that in so doing they are obeying the injunctions of Aristotle. His theory of the nature of matter is contained in his treatise on *Generation and Destruction*. It mainly differed from that of Empedokles in regarding the four “elements” as mutually convertible. Each “element” or principle was regarded as being possessed of two qualities, one of which was shared by another element or principle.

Thus : Fire is hot and dry ; air is hot and wet ; water is cold and wet ; earth is cold and dry.

In each primal “element” one quality prevails. Fire is more hot than dry ; air is more wet than hot ; water is more cold than wet ; earth is more dry than cold. The relative proportion and mutual working of these

qualities determined the specific character of the "element." Thus, if the dryness of fire is overcome by the moisture of water, air is produced ; if the heat of air is overcome by the coldness of earth, water is formed ; if the moisture of water is overcome by the dryness of fire, earth results. Ancient chemical literature contains many illustrations or diagrams symbolising the convertibility or mutual relations of the four "elements."

It has been frequently stated that the influence of the Peripatetic philosophy has been inimical to the development of science. But, in reality, the founder of that school, a descendant of Esculapius, and undoubtedly one of the greatest and most enlightened thinkers of antiquity, was an ideal man of science. This is abundantly evident from such of his works as can be proved to be genuine. Much of what is called Aristotelianism is entirely foreign to the spirit of the teaching of Aristotle. The Aristotelians of the Middle Ages were mainly dialecticians, and almost wholly concerned with the formulæ of syllogistic inference, and without real sympathy with, or knowledge of, his system. Much, too, that was attributed to him, and which was venerated accordingly, is undoubtedly spurious. The fame of the Master has consequently suffered at the hands of those who, calling themselves Peripatetics, were in no proper sense followers of his method or interpreters of his dogma. Aristotle affirmed that natural science can only be founded upon a knowledge of facts, and facts can only be ascertained through observation and experiment. He illustrates this particularly by a reference to astronomy, "which," he says, "is based on the observation of astronomical phenomena, and it is the case with every branch of

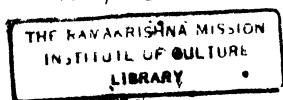
science or art." It is erroneous and unjust, therefore, to suppose that Aristotle's philosophy, as he taught it, is opposed to the true methods of science.

A knowledge of Aristotle's works was transferred by Byzantine writers to Egypt; and, when that land was overrun by the Arabs in the seventh century, they adopted his system, spreading it abroad wherever their conquests extended. In the eighth century they carried it into Spain, where it flourished throughout their occupation of that country. From the ninth to the eleventh century the greater part of Europe was in a state of barbarism. The Moslem caliphate in Spain, under the beneficent rule of Jusuf and Jaküb, alone preserved science from extinction. Cordova, Seville, Grenada, and Toledo were the chief seats of learning in Western Europe; and it was mainly through "the perfect and most glorious physicist," the Moslem Ibn-Roshd—better known as Averroes—(1126–1198), that Christian scholiasts like Roger Bacon acquired their knowledge of the philosophical system of Aristotle, and mainly through the Moslems Geber and Avicenna that they gained acquaintance with the science of the East.

The conception that matter is made up of particles or *atoms*, and that these particles are in a state of ceaseless motion, is to be met with in Hindu and Phœnician philosophy. It was taught by Anaxagoras, Leukippos, and Demokritos to the Greeks, and by Lucretius to the Romans. Leukippos and Demokritos explained the creation of the world as due solely to physical agencies without the intervention of a creative intelligence. According to their theories, the atoms are variable not only in size, but in weight. The smallest atoms are also the lightest. Atoms are impenetrable; no two atoms can simultaneously occupy the same place. The

collision of the atoms gives them an oscillatory movement, which is communicated to adjacent atoms, and these, in their turn, transmit it to the most distant ones. Anaxagoras taught that every atom is a world in miniature, and that the living body is a congeries of atoms derived from the aliments which sustain it. Plants are living things, endowed like animals with respiratory functions, and, like them, atomically constituted. This philosopher was so far in advance of his age that his countrymen accused him of sacrilege, and he only escaped death by flight. Further, the assumption that these atoms exert mutual attractions and repulsions is probably as old as the fundamental conception itself. At least, so far as can be traced, the conceptions of atoms and atomic motion are indissolubly connected. This is not the place to develop the subsequent history of the doctrine of the atom, nor need we now concern ourselves with the old metaphysical quibble of its divisibility or indivisibility. It may be, as Lucretius said, that the original atom is very far down. It may be that the physical atom is something which *is* not divided, not something that *cannot* be divided. This theory, dimly perceived in the mists of antiquity, has grown and strengthened with the ages, and in its modern application to the facts of chemistry has acquired a precision and harmony unimagined even by the poets and thinkers of old. We shall see later how the whole course of the science has been controlled, illumined, and vivified by it. It is not too much to say that the chemistry of to-day is one vast elaboration of this primeval doctrine.

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## CHAPTER III.

### ALCHEMY

ALTHOUGH the intellectual tendencies of the Hellenic mind were hardly calculated to favour the development of chemistry as a science, the speculations of the Greeks concerning the essential nature of matter and the mutual convertibility of the "elements" led incidentally to an extension of the art of operative chemistry. This extension resulted from attempts to realise what was the logical outcome of the teaching of their philosophers—viz., the possibility of the transmutation of metals. The idea of transmutation has its germ in the oldest systems of philosophy. It was a plausible doctrine, not wholly unsupported by the phenomena of the organic world; and it naturally commended itself to men who were only too prone to adopt what their cupidity and love of wealth predisposed them to believe.

It has been assumed that alchemy at no time in its history had the slightest claim to a philosophical foundation, but that its professors and adepts, even at the outset, consciously traded on the credulity and greed of their dupes. Much may be urged against such a partial view. The supposition is not consistent with history or with evolutionary tendencies. It may be, as Davy once said, that "analogy is the fruitful parent of error"; but the idea that metals could be modified—could even be changed one into the other—seemed to find support in innumerable chemical phenomena well-known but imperfectly understood. The fact that

alchemy—that is, the profession of making gold from other metals—came to be practised by rogues is no proof that it never had, and never could have had, a philosophical basis.

The changes which substances experience under the influence of fire, air, and water, or as the result of their action on each other, are frequently so profound that even the most superficial of the early observers of chemical processes could not fail to be impressed by them. Many of these changes are, in fact, far more striking as regards alteration in outward characters—such as colour, lustre, density, etc.—than are the differences between individual metals; say, between lead and tin, or between tin and silver, or between brass and gold. That copper ores, by appropriate treatment with other ores, or that copper itself by the addition of another metal, could be made to furnish a metallic-looking substance having certain of the attributes of gold was known to the earliest workers in metals. What is thought to be the oldest chemical treatise in existence is a papyrus in the possession of the University of Leyden. It consists of a number of receipts for the working of metals and alloys, and describes methods of imitating and falsifying the noble metals. It explains how, by means of arsenic, a white colour may be given to certain metals, and how, by the addition of cadmia, copper acquires the colour of gold. The same papyrus describes a method of blackening metals by the use of preparations of sulphur. The limited knowledge of chemical phenomena and of chemical processes which these early workers necessarily possessed, so far from precluding a belief in the possibility of transmutation, actually encouraged it. As nothing was known of the true nature of brass,



or of its exact relation to copper, it was not unreasonable to suppose that, if this substance could be made to acquire *some* of the attributes of gold by a process essentially chemical, processes of a like nature might cause it to acquire, if not *all*, at least so many of them as to enable it to pass for gold of greater or less fineness. To them, as to us, perfection was, in technical practice, a question of degree: the very language of the metallurgists of old was in this respect nowise different from that of the metallurgists of to-day.

It is not necessary to suppose that these early attempts were deliberately and consciously fraudulent, like those of coiners who knowingly seek to make an alloy of lead and tin simulate silver. The first alchemists sought in good faith to make something which should be of the true nature and essence of gold as they conceived it to be. In fact, the idea of transmutation had a rational foundation in a theory of the intrinsic nature of metals which may be looked upon as a development of the ancient beliefs concerning the essential nature of all forms of matter.

Just as the Aristotelian "elements" were qualities which, according to their degree,<sup>1</sup> determined the nature of substances, so, in like manner, the specific character of a metal depended upon the relative proportion of its "sulphur" and "mercury." These terms had no certain reference to what we to-day understand by sulphur and mercury. They denoted simply qualities. The essence or "element" of mercury conferred lustre, malleability, ductility, and fusibility, or, speaking generally, the properties which we connote as metallic; while to the essence or "element" of sulphur was to be attributed the combustibility—or, speaking generally, the alterability—of

the metal by fire. By modifying the relative proportion of these constituent elements, or by purifying them from extraneous substances by the operations of chemistry, it was conceived that the several metals could be changed one into the other. To effect this purification it was necessary to add various preparations known as "medicines," chief among which was the *Great Elixir*, or *Magisterium*, or the *Philosopher's Stone*, by which the final transformation into the noblest of the metals could alone be achieved.

The Arabic words *kimyâ* and *iksir* were originally synonymous, and each was used to denote the agent by which the baser metals could be transmuted into silver and gold. Ultimately the former term became restricted to indicate the art of transmutation (alchemy), whereas *iksir*, or *al-iksir*, continued to denote the medium by which the transmutation was effected. By later writers the term was used to indicate a liquid preparation—the *quintessence of the philosophers*—whence we have the word *elixir*, which always means a liquid.

The alchemistic theory of the compound nature and mutual relations of the metals is usually ascribed to Geber; but, although he adopted it, he distinctly states that it did not originate with him, but that he found it in the writings of his predecessors.

The idea of the *stone*, the *philosophical powder*, the *grand magisterium*, the *elixir*, the *tincture*, the *quintessence*—by all of which terms the transmuting medium is known in the literature of alchemy—is probably connected with another conception respecting the origin of metals which can be traced to very early times, and was prevalent throughout the Middle Ages. It was supposed of old that metals were *generated* within the earth, as animals and plants were generated on its

surface, and that something akin to a seed, or semen, was needed to initiate their formation. The great problem of alchemy was to discover this fecundating substance, as upon it depended the genesis of the perfect metal. This idea of the conception of metals runs through the literature of alchemy. It explains many allusions and much of the terminology of its writers. For example, the furnace in which the alchemist makes his projection is constantly spoken of as the *philosophical egg*.

It is impossible to say with certainty when and where the art of alchemy originated. There is no evidence that it has the antiquity which certain of its adepts claimed for it. Oleus Borrichius referred it to the time of Tubal-cain. The earliest writers on alchemy were probably Byzantine ecclesiastics, some of whom professed to ascribe the art to Egypt, and eventually to the mythological deity Hermes, whose association with chemistry in such terms as "the hermetic art," "hermetically sealed," etc., is thus explained.

This much is established—that at some period prior to the tenth century there arose a special class of operative chemists, for the most part more learned in the knowledge of chemical phenomena in general, and more skilled in chemical manipulation, than the craftsmen and artisans engaged in the manufacture of technical products. They devoted themselves to searching for methods whereby the common and baser metals might be converted into silver and gold. The first known definition of chemistry relates to the aim and operations of this special class. It occurs in the lexicon of Suidas, a Greek writer of the eleventh century, who defines chemistry, *χημεία*, as the preparation of silver and gold. Attempts at the artificial preparation of the

noble metals probably originated with the Arabians, who followed the Egyptians and the Greeks in the cultivation of chemical pursuits.

Neither Hesiod nor Homer makes mention of the art of producing gold from any other metal, or speaks of the universal medicine. Nor are they referred to by Aristotle or by his pupil Theophrastus. Pliny nowhere speaks of the philosopher's stone, although he tells the story of Caligula, who, tempted by his avarice, sought to make gold from orpiment (*auripigmentum*) by distillation. "The result was that he did indeed obtain gold, and of the finest kind; but in so small quantity, and with so much labour and apparatus, that, the profit not countervailing the expense, he desisted."

According to Boerhaave, the first author who mentions *al-chemia* is Julius Firmicus Maternus, who lived under Constantine the Great, and who, in his *Mathesis*, c. 15, speaking of the influences of the heavenly bodies, affirms "that, if the moon be in the house of Saturn when a child is born, he shall be skilled in alchemy."

The first writer who mentions the possibility of transmuting metals would appear to be a Greek divine called Æneas Garæus, who lived towards the close of the fifth century, and who wrote a commentary on Theophrastus. He was followed by Anastatius the Sinaite, Syncellus, Stephanus, Olimpiodorus; and, says Boerhaave, "a crowd of no less than fifty more, all Greeks, and most or all of them monks." "The art seemed now confined to the Greeks, and among them few wrote but the religious, who from their great laziness and solitary way of life were led into vain, enthusiastical speculations, to the great disservice and adulteration of the art. .... They all wrote in the natural style of the Schoolmen, full of jargon, grimace, and obscurity."

Experimental alchemy, as distinguished from industrial chemistry, may, as already stated, be said to have originated with the Arabians. At first, alchemy was regarded as a branch of the art of healing, and its professors were invariably physicians who occupied themselves with the preparation of chemical medicines. In fact, in the beginning its true aim was regarded as that which Paracelsus and the school of iatro-chemists subsequently defined it to be. Under the rule of the Caliphs the study of chemistry made considerable progress, and its literature was greatly augmented. The most notable name in the history of chemistry during the eighth century was **Abu-Moussah-Dschabir-Al-Sufi**—otherwise **Geber**—(born 702, died 765), who is stated to have been either a native of Mesopotamia, or a Greek and a Christian, who afterwards embraced Mahometanism, went to Asia, and acquired a knowledge of Arabic. According to Leo Africanus, a Greek who wrote of the antiquity of the Arabs, Geber's book was originally written in Greek and translated thence into Arabic, and he was not known by the name Geber, which signifies a *great man* or a *prince*, till after this version. Latin translations of what purported to be his works were first published in the early part of the sixteenth century, and an English rendering appeared in 1678. According to this it would seem that Geber regarded all the metals as compounds of "sulphur" and "mercury," the differences between them depending upon the relative proportion and degree of purity of these constituents. He is said to have distinguished them by the astrological names of the planets: thus gold became *Sol*, silver *Luna*, copper *Venus*, iron *Mars*, tin *Jupiter*, and lead *Saturn*. That an occult connection of the metals with the stars existed was part of the creed of alchemy, and

the influence of that belief is still traceable in chemical, and especially in pharmaceutical, literature; as, for example, in such terms as *Lunar caustic*, *Martian preparations*, *Saturnine solutions*, etc.

It has been held that the idea of a universal medicine had its origin with Geber. But this may be due to a misreading of his words, which in reality may have reference to the transmutation of metals. He tells of a medicine which cures all lepers. But this may be nothing but allegory. By *man* is probably meant gold, and by *lepers* the other metals; and the medicine is the universal solvent or agent which transmutes. Alchemistic literature is full of allegories of this character. Berthelot has shown that in reality there were two Gebers—one who is generally considered to be of Arab origin, and another whose identity is not established, but who was probably a Western European who appears to have lived about the year 1300.<sup>1</sup>

Other notable names in the history of Arabian alchemy are **Rhazes**, or **Abû Bakr Mohammed ibn Zakariyâ el-Râzi**, who lived *circa* 925, and **Avicenna**, or in Arabic **Abû Ali el-Hosein ibn-Abdallah ibn-Sina**, born 980, died 1037. The former, a Persian, practised medicine at Baghdad as a follower of Galen and Hippocrates. The latter, one of the most eminent of Moslem physicians and a voluminous writer, was a native of Bokhara. He is mainly known in the history of science by his *Canon of Medicine*, in which he describes the composition and preparation of remedies.

<sup>1</sup> There is very little doubt that the work of "Phileletha," which professed to be taken from an "Uhralten MS." preserved in the Vatican Library, entitled *Geberi des Königes der Araber*, and published by Hieron. Philipp. Nitschel, Frankfurth and Leipzig, in 1710, is spurious.

He wrote at least one treatise on alchemy, but others attributed to him are probably apocryphal. Of his *Philosophia Orientalis*, mentioned by Roger Bacon and Averroes, no trace remains.

Although it is reasonably certain that the alchemists of the time of Geber and of his successors had a considerable acquaintance with manipulative chemistry, there were so many impudent literary forgeries during the alchemical period that the precise extent of the knowledge possessed by the early chemists must always remain uncertain.

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A number of the ordinary chemical processes, such as distillation, sublimation, calcination, filtration, appear to have been known to, and to have been commonly practised by, the Arabian chemists; and many saline substances, such as carbonate of soda, pearlash, sal-ammoniac, alum, copperas, borax, silver nitrate, cinnabar, and corrosive sublimate, were prepared by them. They seem to have known of certain of the mineral acids, and were familiar with the solvent properties of *aqua regia*.

An examination of the literature of alchemy serves to show how its principles and tenets developed. The philosopher's stone is first heard of in the twelfth century. Prior to that period the greater number of the Greek and Arabian writers contented themselves with affirming the fact of transmutation, without indicating how it might be accomplished. The universal medicine and the elixir of life were the products of a later age; no mention of them is known before the thirteenth century.

Alchemy flourished vigorously during the Middle Ages, and lingered on even until the early part of the nineteenth century. Its history is simply a long chapter

in the history of human credulity. For the most part it is a record of self-deception, imposture, and fraud. It produced an abundant literature, mainly the work of ecclesiastics, between the seventh and fourteenth centuries; but as regards the artificial preparation of the noble metals or the discovery of the universal medicine or the elixir of life it was barren of result.

Although no clear line of demarcation is possible, it may be convenient, in dealing with the personal history of alchemy, to divide it into the two periods before and after Paracelsus, since under his inspiration and example alchemy underwent a great development as regards its professed objects. These eventually became so extravagant that, wide as are the limits of human credulity, its pretensions gradually brought it into disrepute, and it fell by the weight of its own absurdities.

One of the most reputable of the early Western alchemists was **Albert Groot**, or **Albertus Magnus**, born at Lauingen in 1193. He was a Dominican monk, who became Bishop of Regensburg, but, resigning his bishopric, retired to a convent at Cologne, where he devoted himself to science until his death in 1282. He is credited with having written a number of chemical tracts, for the most part in clear and intelligible language, which is more than can be said of the greater portion of alchemistical literature. He gives an account of the origin and main properties of the chemical substances known in his time, and describes the apparatus and processes used by chemists, such as the water-bath, alembics, aludels, and cupels. He speaks of cream of tartar, alum and caustic alkali, red lead, liver of sulphur and arsenic, green vitriol and iron pyrites.

Contemporaneously with him was **Roger Bacon**,



*Doctor Mirabilis*, one of the most erudite men of his age, who was born near Ilchester in Somerset in 1214, and, after studying at Oxford, became a friar, occupied himself in philosophical pursuits, and wrote numerous tracts on alchemy. He describes what was probably gunpowder, but there is no certain proof that he invented it. In his *De Secretis Artis et Naturæ*, written before 1249, he gives instructions for refining saltpetre, and in an anagram which Colonel Hime, in his *Gunpowder and Ammunition*, has interpreted, he states that a mixture "which will produce a thundering noise and a bright flash" may be made by taking "7 parts of saltpetre, 5 of young hazelwood, and 5 of sulphur." He died in 1285.

**Raymund Lully**, a friend and scholar of Bacon, was born in Majorca in 1225 (others say 1235), and was buried there in 1315. A member of the Order of Minorites, he had a great reputation as an alchemist; and a number of books on alchemy and chemical processes are ascribed to him. He described modes of obtaining nitric acid and aqua regia, and studied their action upon metals. He obtained alcohol by distillation, and knew how to dehydrate it by the aid of carbonate of potash, which he obtained by calcining cream of tartar. He prepared various tinctures and essential oils, and a number of metallic compounds, such as red and white precipitate. To him is usually ascribed the first idea of a universal medicine.

There is some difficulty in believing that all that is ascribed to Lully was actually the work of his age, for it would appear to have been a common practice with the disciples and followers of a notable scholar to usher in their performances under their master's name—a practice not unknown in later days. "So full are they of the

experiments and observations which occur in our later writers that either the books must be suppositious, or the ancient chemists must have been acquainted with a world of things which pass for the discoveries of modern practice" (Boerhaave). The story is that Lully plunged into the study of chemistry from the desire to cure a maiden of a cancered breast, and that he was stoned to death in Africa, whither he had journeyed as a missionary. It has been further alleged that at one period of his life he made gold in the Tower of London by the King's order, and that he offered Edward III. a supply of six millions to make war against the infidels. As Boerhaave drily remarks, "the history of this eminent adept is very much imbroiled."

**Arnoldus Villanovanus**, or **Arnaud de Ville-neuve**, a Frenchman, is said to have been born in 1240, and to have practised medicine in Barcelona, where he incurred the enmity of the Church by reason of his heretical opinions, and was obliged to leave Spain. He led a wandering life, eventually settling in Sicily, under the protection of Frederick II., and acquired a great reputation as a physician. Summoned thence by Clement V., who lay sick at Avignon, he lost his life by shipwreck in 1313.

**Johannes de Rupecissa**, or **Jean de Raquetaillade**, a Franciscan friar who lived from about the middle to the end of the fourteenth century, wrote a number of treatises on alchemy, and described methods of making calomel and corrosive sublimate. He was accused of the practice of magic, and, by order of Innocent VI., was thrown into prison, where he died. He was buried at Villefranche.

**George Ripley**, an Englishman, Canon of Bridlington, practised alchemy during the second half of

the fifteenth century. He spent some time in Italy in the service of Innocent VIII. On his return to England he became a Carmelite, and died in 1490. Like Bacon, he was charged with magic. According to Mundanus, he followed alchemy with such success that he was able to advance to the knights of St. John of Jerusalem large amounts of gold for the defence of the Isle of Rhodes against the Turks.

One of the most important names in connection with the history of alchemy is that of **Basil Valentine**. Of his personal history nothing is known. He was supposed to be a Benedictine monk who lived in Saxony during the latter half of the fifteenth century; but there are grounds for the belief that the numerous writings attributed to him are in reality the work of various hands. The attempt made by Maximilian I. to discover the identity of the author was unavailing, nor have subsequent inquiries had any better result. The collection of books bearing his name, first published in the beginning of the seventeenth century, reveals quite a remarkable number of chemical facts up to that time not generally known. The most important of these relate to antimony and its preparations, such as butter of antimony, powder of algaroth, oxide of antimony, etc. He seems to have known of arsenic, zinc, bismuth, and manganese. He describes a number of mercurial preparations, and many of the salts of lead were known to him. He mentions fulminating gold, and was aware that iron could be coated with copper by immersion in a solution of blue vitriol. He knew of green vitriol and the double chloride of iron and ammonium, and gave the modes of making a considerable number of other metallic salts, such as the *sal armoniacum*, which we now know as sal ammoniac. He

also appears to have prepared ether and the chloride and nitrate of ethyl.

There is reason to believe, as stated already, that many of the published works ascribed to these learned men are the work of obscure individuals who traded on their fame. What may with certainty be credited to them serves to show that their theoretical opinions had much in common. They all regarded the transmutation of metals and the existence of the philosopher's stone as facts which could not be controverted. They followed Geber in assuming that all the metals were essentially compound in their nature, and consisted of the essence or "element" of mercury, united with different proportions of the essence or "element" of sulphur.

The alchemists were the professional chemists of their time, and many of them were practising physicians. Indeed, professional chemistry may be said to have originated out of the practice of physic. As the number of chemical products increased and their value in therapeutics became more and more appreciated, there arose another school of alchemists, whose energies were devoted, not to the transmutation of metals—which, however plausible as a belief, seemed hopeless of achievement—but to the more immediate practical benefits which it was recognised must follow from the closer association of chemistry and medicine. This school came to be known as the iatro-chemists. As their doctrines exercised a great influence upon the development of chemistry, it will be desirable to treat of them and their professors in a special chapter.

## CHAPTER IV:

### THE PHILOSOPHER'S STONE

DURING the fourteenth, fifteenth, and sixteenth centuries the cult of alchemy attained to the dignity of a religion. Belief in transmutation and in the virtues and powers of the philosopher's stone, in the universal medicine, the alkahest, and the elixir of life, formed its articles of faith. The position it acquired was due to some extent to the attitude towards it of the Romish Church. Many reputable bishops and fathers were professed alchemists; and chemical laboratories, as in the Egyptian temples, were to be found in monasteries throughout Christendom. Pope John XXII., who had a laboratory in his palace at Avignon, is the reputed author of a work, *Ars Transmutatoria*, published in 1557. But to a still larger extent it was due to the fact that alchemy appealed to some of the strongest of human motives—the wish for health, the fear of death, and the love of wealth. It was a cunningly devised system, which exploited the foibles and frailties of human nature. The policy of the Church, however, it should be said, was not consistently and uniformly favourable to alchemy. Its practices occasionally came under the papal ban, although at times, to suit the exigencies of Christian princes, the interdict was removed. Theosophy and mysticism were first imported into alchemy, not by Arabs, but by Christian workers. The intimate association of religion with alchemy during the Middle Ages is obvious in the writings of Lully, Albertus

Magnus, Arnaud de Villeneuve, Basil Valentine, and other ecclesiastics. Invocations to divine authority are freely scattered over their pages. Even the lay alchemist professed to rule his life and conduct by the example and precepts of the good Bishop of Regensburg. He was directed to be patient, assiduous, and persevering; discreet and silent; to work alone; to shun the favour of princes and nobles, and to ask the divine blessing on each operation of trituration, sublimation, fixation, calcination, solution, distillation, and coagulation.

Although alchemy, at least in its decadent days, lived for the most part by its appeal to some of the lowest instincts of mankind, and is only worth notice as a transient phase in the history of science, a few details concerning the tenets and practices of its professors may be of interest to the curious reader. And first as regards the nature of the philosopher's stone—the grand magistery, the quintessence. Many alchemists professed to have seen and handled it. It is usually described as a red powder. Lully mentions it under the name of *Carbunculus*. Paracelsus says that it was like a ruby, transparent and brittle as glass; Berigard de Pisa that it was of the colour of a wild poppy, with the smell of heated sea salt; Van Helmont that it was like saffron, with the lustre of glass. Helvetius describes it as of the colour of sulphur. Lastly, an unknown writer, under the pseudonym of "Kalid," says that it may be of any colour—white, red, yellow, sky-blue, or green. As the substance was wholly mythical, a certain latitude of description may reasonably be expected. Some of the alchemists were of opinion that the magistery was of two kinds—the first, the *grand* magistery, needed for the production of gold;

the second, the *small* magistery, only capable of ennobling a metal as far as the stage of silver. Then, as to the amounts required to effect a transmutation, accounts are equally discrepant. Arnaud de Villeneuve and Rupescissa assert that one part of the grand magistery will convert a hundred parts of a base metal into gold; Roger Bacon, a hundred thousand parts; Isaac of Holland, a million. Raymond Lully states that the philosopher's stone is of such power that even the gold produced by means of it will ennoble an infinitely large amount of a base metal.

It is hardly necessary to state that a preparation of such potency is capable of effecting anything or everything; and accordingly, as time went on, other attributes than that of transmutation came to be associated with it. It may be, as Boerhaave surmises, that the idea of a universal medicine had its origin in a too literal interpretation of Geber's allegory of the six lepers. Be this as it may, during the fourteenth and fifteenth centuries the philosopher's stone was gravely prescribed as a means of preserving health and prolonging life. In case of illness one grain was directed to be dissolved in a sufficient quantity of good white wine, contained in a silver vessel, the draught to be taken after midnight. Recovery would follow after an interval depending upon the severity and age of the complaint. To keep in good health, the dose was to be repeated at the beginning of spring and autumn. "By this means," says Daniel Zacharias, "one may enjoy perfect health until the end of the days assigned to one." Isaac of Holland and Basil Valentine are equally explicit, but in their case it is recommended that the dose should be taken once a month: thus life would be prolonged "until the supreme hour fixed by the king of heaven."

Other alchemists were not always so prudent in prophecy. Artephius gave the limit of human life thus prolonged as a thousand years; Gualdo, a Rosicrucian, was stated to have lived four hundred years. Raymond Lully and Salomon Trismosin, we are told, renewed their youth by means of it. The advanced age at which Noah begat children could only be due, says Vincent le Beauvais, to his use of the philosopher's stone. Dickinson wrote a learned book to prove that the great age of the patriarchs was owing to the same secret.

But not only were health and length of days the fortunate lot of him who possessed the philosopher's stone; increase of wisdom and virtue equally followed from its use. As it ennobled metals, so it freed the heart from evil. It made men as wise as Aristotle or Avicenna, sweetened adversity, banished vain-glory, ambition, and vicious desires. Adam received it at the hands of God, and it was given also to Solomon, although the commentators were rather exercised to know why, as he possessed the philosopher's stone, he should have sent to Ophir for gold.

It would serve no good purpose to attempt to describe the recipes given by various alchemists to prepare this precious substance. With an affectation at times of precision, they were purposely obscure, and always enigmatical. As Boyle said of them, they could scarcely keep themselves from being confuted except by keeping themselves from being clearly understood. One example of their recipes must suffice: "To fix quicksilver.—Of several things take 2, 3 and 3, 1; 1 to 3 is 4; 3, 2 and 1. Between 4 and 3 there is 1; 3 from 4 is 1; then 1 and 1, 3 and 4; 1 from 3 is 2. Between 2 and 3 there is 1, between 3 and 2 there is 1. 1, 1, 1, and



1, 2, 2 and 1, 1 and 1 to 2. Then 1 is 1. I have told you all." No wonder, after an equally luminous explanation, a pupil of Arnaud de Villeneuve should have exclaimed: "But, master, I do not understand." Upon which the master rejoined that he would be clearer another time.

Nor is it necessary to dilate upon the other virtues which were ascribed at various times to the philosophical powder, as, for example, its power of making pearls and precious stones, or of its use in preparing the *alkahest*, or universal solvent, invented by Paracelsus. In their attempts to fathom the depths of human credulity the alchemists at length over-reached themselves. The idea of a universal solvent carried with it, as Kunkel pointed out, its own refutation: if it dissolved everything, no vessel could contain it. And yet, says Boerhaave, a whole library could be filled with writings by the school of Paracelsus on the *alkahest*. From the latter end of the sixteenth century repeated attempts were made to expose the pretensions and demonstrate the absurdities of alchemy. Among its adversaries may be cited Thomas Erastius, Hermann Conringius, and the Jesuit Kircher. Many of their dupes, potentates and princes who were powerful enough to exercise it, occasionally visited with their vengeance those who, unmindful of the injunctions of Albert the Great, had traded too long upon their credulity. The Emperor Rudolph II., who earned the title of "The Hermes of Germany," was a zealous cultivator of alchemy, and had a well-equipped laboratory in his palace at Prague, to which every adept was welcome. Ferdinand III. and Leopold I. were also patrons of the hermetic art, as were Frederick I. and his successor, Frederick II., Kings of Prussia. Indeed,

at one period nearly every Court in Europe had its alchemist, with the privileges of the Court fool or the poet laureate. The fraud and imposture to which the practice gave rise led occasionally to the promulgation of stringent laws against it, and at times the pursuit of operative chemistry became well-nigh impossible in some countries. In the fifth year of the reign of Henry IV. (1404) it was enacted that "None from henceforth shall use to multiply gold or silver, or use the craft of multiplication; and if the same do he shall incur the pain of felony." According to Watson, the true reason for passing this Act was not an apprehension that men should ruin their fortunes by endeavouring to make gold, but a jealousy lest Government should be above asking aid of the subject. At the same time, letters patent were granted to several persons, permitting them to investigate the universal medicine and perform the transmutation of metals.

Alphonse X., of Castille, the author of the *Key of Wisdom*, practised alchemy. Henry VI., of England, and Edward IV. had dealings with adepts. Even Elizabeth Tudor, who was a shrewd enough sovereign, had the notorious Dr. Dee in her pay. Charles VII. and Charles IX., of France, Christian IV., of Denmark, and Charles XII., of Sweden, sought to replenish their exhausted treasuries by the aid of the philosopher's stone. If princes eventually learned not to put their trust in alchemists, alchemists learned equally to their cost not to put their trust in princes. Duke Julius, of Brunswick, in 1575, burnt a female alchemist, Marie Ziglerin, who had failed in her promise to furnish him with a prescription for the making of gold. David Benthler killed himself to escape the fury of the Elector Augustus, of Saxony. Bragadino was hanged at

Munich in 1590 by the Elector of Bavaria. Leonard Thurneysser, who gained an evil notoriety in his day as one of the most unscrupulous of the followers of Paracelsus, and who amassed considerable wealth by the sale of cosmetics and nostrums, was deprived of his ill-gotten gains in 1584 by the Elector of Brandenburg, and died in misery in a convent. Borri, a Milanese adventurer, who had deceived Frederick III., of Denmark, was imprisoned for years by that monarch, and died in captivity in 1695. William de Krohnemann was hanged by the Margrave of Beyreuth, who, with grim irony, caused the inscription to be fixed to his gibbet: "I once knew how to fix mercury, and now I am myself fixed." Hector de Klettenberg was beheaded in 1720 by Augustus II., King of Poland.

All the followers of Hermes were not so wary or so candid as the artist who declined an invitation to visit the Court of Rudolph II., saying: "If I am an adept, I have no need of the Emperor; if I am not, the Emperor has no need of me." Well might John Clytemius, Abbot of Wiezenberg, write: "*Vanitas, fraus, dolus, sophisticatio, cupiditas, falsitas, mendacium, stultitia, paupertas, desesperatio, fuga, proscriptio et mendicitas, perdisæque sunt chemiæ.*"

Despite the attacks of Kunkel, Boerhaave, the elder Geoffroy, Klaproth, and other chemists of influence and repute, alchemy died hard. It found believers in England until near the close of the eighteenth century, and was professed even by a Fellow of the Royal Society—Dr. James Price, of Guildford, who, in chagrin at the exposure of his pretensions, put an end to his existence in 1783. Hermetic societies existed in Westphalia, at Königsberg, and at Carlsruhe down to the first decade of the nineteenth century. M.

Chevreul, who lived well into that century, relates that he knew of several persons who were convinced of the truth of alchemy, among them "generals, doctors, magistrates, and ecclesiastics." The strange medley of alchemy, theosophy, thaumaturgy, and cabalisticism professed by Christian Rosenkreuz is not without its adherents, even in this twentieth century.

If the baser metals have not been made to furnish gold, truth at least has followed from the practice of error. This is the only transmutation which the art of Hermes has succeeded in effecting. To err is human. Although alchemy is not without its special interest as one of the most remarkable aberrations in the history of science, some of its practitioners, it must be admitted, deceived only themselves: if misguided, they were at least honest, and pursued their calling in a settled conviction of the soundness of their faith. Although they never reached their goal—the discovery of the Philosopher's Stone and the Elixir of Life—their labours were not wholly vain, for many new and unexpected facts came to light as the result of their assiduity.

"Credulity in arts and opinions," wrote Lord Bacon in *De Augmentis Scientiarum*,

is likewise of two kinds—viz., when men give too much belief to arts themselves, or to certain authors in any art. The sciences that sway the imagination more than the reason are principally three—viz., astrology, natural magic, and alchemy.....Alchemy may be compared to the man who told his sons that he had left them gold, buried somewhere in his vineyard; while they by digging found no gold, but by turning up the mould about the roots of the vines procured a plentiful vintage. So the search and endeavours to make gold have brought many useful inventions to light.

## CHAPTER V.

### IATRO-CHEMISTRY

**THE** term "iatro-chemistry" denotes a particular phase in the history of medicine and of chemistry. The iatro-chemists were a school of physicians who sought to apply chemical principles to the elucidation of vital phenomena. According to them, human illnesses result from abnormal chemical processes within the body, and these could only be counteracted by appropriate chemical remedies. Although this idea did not originate with him, the chief exponent of this school is commonly said to be Paracelsus.

A man of violent passions, coarse, drunken, arrogant, and unscrupulous, **Philippus Aureolus Theophrastus Paracelsus Bombastus von Hohenheim**—to give him his full name—would seem to have possessed none of the attributes needed by the successful leader of an intellectual revolution.

Born at Etzel in Switzerland in 1493, the son of a physician, William Bombast von Hohenheim, who combined the practice of astrology with that of alchemy, Paracelsus, even as a youth, became a wanderer, passing from province to province and cloister to cloister, living by telling fortunes and practising sometimes as a quack and at other times as an army surgeon, and gaining, as he tells us, much curious information from old women, gipsies, conjurers, and chemists. If we may trust his own account of himself, he had, before he was thirty-three, wandered over the whole of Europe,

and even into Africa and Asia, everywhere performing miraculous cures and constantly getting into trouble. In 1526 he secured the appointment of Professor of Physic in the University of Basle, and signalled his occupancy of the chair by a course of lectures—a farrago of confused German and barbarous Latin—in which he assailed with extraordinary vigour and unexampled coarseness the medical system of the school of Galen. Scandalised as his professional brethren might be, Paracelsus expressed, intentionally or unintentionally, the feeling of impatience with which the laity viewed a system of therapeutics based only on tradition. In this revolt against authority he initiated a movement which, whatever might have been its influence on medicine, served eventually, under the guidance of worthier men, to emancipate chemistry from the thralldom of alchemy.

Paracelsus did little more than initiate. Although his many tracts show that he was familiar with nearly every chemical preparation of his time, many of which he used in his practice, he added no new substance to science. A man of great ability and extraordinary talent, he squandered his powers in dissipation. His intemperate conduct soon lost him his chair at Basle; and, after an ignoble quarrel with the magistracy, he fled the town, and, resuming his wandering life, died, under wretched circumstances, at Salzburg, in his forty-eighth year.

Space will not permit of any account of the philosophical opinions of Paracelsus—of his mysticism, his theosophy, his pantheism, his extraordinary doctrine of the Archæus and Tartarus, his association of astrology with medicine. His chief merit lies in his insistence that the true function of chemistry was not to make

gold artificially, but to prepare medicines and substances useful to the arts. He thereby made chemistry indispensable to medicine, and thenceforward chemistry began to be taught in the universities and in the schools as an essential part of a medical education.

Paracelsus is usually regarded as a typical alchemist—the kind of man made familiar to us by the paintings of Teniers, Van Ostade, and Stein—a boorish, maudlin knave, who divided his time between the pothouse and the kitchen in which he prepared his extracts, simples, tinctures, and the other nostrums which he palmed off upon a credulous world, as ignorant and superstitious as himself. There is much in the personal history of Paracelsus that serves to justify such a view of him. That he was in the main an impudent charlatan, ignorant, vain, and pretentious, there can be little doubt. He had an astonishing audacity and a boundless effrontery; and it was largely by the exercise of these qualities that he secured such professional success as he enjoyed.

To judge from the number of the published works associated with his name, he was an active and industrious writer. Considering that during the greater part of his waking time he was more or less intoxicated it is difficult to conceive what opportunity he had for composing them. Only one or two are known to be genuine. These, according to Operinus, his publisher he dictated; and from their incoherence and obscurity, their mystical jargon, and misuse of terms, they read like the ravings of one whom drunkenness had deprived of reason. Many of the tracts and larger works appeared after his death—some of them years after; and there is no certain proof that he was the actual author. Even if we regard them as supposititious, the fact that they

should be published under his name is significant of the influence and notoriety which this extraordinary man succeeded in achieving during his short and chequered career.

The immediate followers of Paracelsus—among whom may be named Thurneysser, Dorn, Severinus, Duchesne—distinguished themselves only by the boldness with which they promulgated his doctrines, and the unscrupulous use which they made of his methods. They were all zealous anti-Galenists, who professed to believe that the sum and perfection of human knowledge was to be found in the Cabala, and that the secrets of magical medicine were contained in the Apocalypse. They adopted pantheism in all its grossness: everything that exists eats, drinks, and voids excrement; even minerals and liquids assimilate food, and eliminate what they do not incorporate. Sylphs inhabit the air, nymphs the water, pigmies the earth, and salamanders the fire. Thus even the Aristotelian elements were animated. Mercury, sulphur, and salt were, according to Paracelsus, the primal principles which entered into the composition of all things, material and immaterial, visible and invisible. The following so-called “harmonies” were essential articles of faith with a Paracelsian:—

Soul	Spirit	Body
Mercury	Sulphur	Salt
Water	Air	Earth

The laws of the Cabala were held to explain the functions of the body. The sun rules the heart, the moon the brain, Jupiter the liver, Saturn the spleen, Mercury the lungs, Mars the bile, Venus the kidneys. Gold was a specific against diseases of the heart; the liquor of Luna (solution of silver) cures diseases of the



brain. "The remedies," said Paracelsus, "are subjected to the will of the stars, and directed by them. You ought, therefore, to wait until heaven is favourable before ordering a medicine."

The Paracelsian physicians, for the most part, were a set of dangerous fanatics, who, in their contempt for the principles of Hippocrates, Galen, and Avicenna, and in their reckless use of powerful remedies, many of them metallic poisons, wrought untold misery and mischief. The inevitable reaction set in, and certain of the faculties, particularly that of Paris, prohibited their licentiates, under severe penalties, from using chemical remedies. It is not to be supposed, however, that all iatro-chemists were unscrupulous charlatans. Some of them clearly perceived the significance and true value of the movement which Paracelsus may be credited with having originated.

**Andreas Libavius**, or Libau, originally a physician, born in Halle, is best known by his *Alchymia*, published in 1595, which contains an account of the main chemical facts known in his time, and is written in clear and intelligible language, in strong contrast to the mystery and obscurity of his predecessors. He was the discoverer of stannic chloride, still known as the fuming liquor of Libavius, and described a method of preparing oil of vitriol in principle identical with that now made use of on a manufacturing scale. He died in 1616.

**John Baptist van Helmont**, a scion of a noble Brabant family, was born in Brussels in 1577. After studying philosophy and theology at the University of Louvain, he directed his attention to medicine, and made himself familiar, in turn, with every system from Hippocrates to Paracelsus. Having spent some time in travel, he settled on his estate at Vilvorde, and occupied

himself with laboratory pursuits until his death in 1644. Van Helmont was a scholarly, studious man, and a philosopher. A theosophist and prone to mysticism, he had many of the mental characteristics of Paracelsus, without his fanaticism and overweening egotism. He narrowed the number of Aristotle's elements down to one, and, like Thales, considered water to be the true principle of all things, supporting his theory by ingenious observations on the growth of plants (see p. 16). He first employed the term *gas*, and was aware of the existence of various aeriform substances, anticipating Hales, who has been styled the father of pneumatic chemistry, in the discovery of many gaseous phenomena. He gave an accurate description of carbonic acid gas, which he termed *gas sylvestre*, and showed that it is produced from limestone and potashes in the fermentation of wine and beer, and that it is formed in the body and in the earth. The doctrines of the iatro-chemists were further spread by Sylvius in Holland, and by Willis in England.

**Francis de le Boë Sylvius**, born at Hanau in 1614, became Professor of Medicine in the University of Leyden, where he exercised great influence as a teacher until his death in 1672. Medicine he treated simply as a branch of applied chemistry, and the vital processes of the animal body as purely chemical. He freed the theory of physic from much of the mystical absurdity introduced into it by Paracelsus and van Helmont, and by his practice brought chemical remedies once more into vogue. He was aware of the distinction between venous and arterial blood, and that the red colour of the latter was due to the influence of air. Combustion and respiration he regarded as analogous phenomena.

**Thomas Willis** was born in Wiltshire in 1621, and while a student at Christchurch bore arms in the Royalist army when Oxford was garrisoned for Charles I. In 1660 he became Sedleian Professor of Natural Philosophy, and ultimately settled in London as a physician. He died in 1675, and was buried in Westminster Abbey.

Willis imagined that all vital actions were due to different kinds of fermentation, and that diseases were caused by abnormalities in the fermentative process. Although a Paracelsian as regards his theory of the constitution of matter, he followed Sylvius and his pupil Tachenius in banishing mysticism from medicine. He was a skilful anatomist, and gave the first accurate description of the brain and nerves.

Other notable iatro-chemists were Angelus Sala, Daniel Sennert, Turquet de Mayerne (who became body physician to James I.), Oswald Croll, Adrian van Mynsicht, and Thomas Lieber. Croll introduced the use of potassium sulphate and succinic acid into medicine, and Van Mynsicht that of tartar emetic. Various antimonial preparations had previously been employed by chemical physicians since the time of Basil Valentine, despite the ban of the Parliament of Paris on their use.

The chief service of iatro-chemistry to science consisted in its influence in bringing chemistry within the range of professional study, whereby a great extension in its pursuit was effected, with the result that a largely increased number of substances was discovered. Moreover, this wider experience of chemical processes familiarised workers with chemical phenomena in general, and thereby contributed to lay the foundations of a general theory of chemical action, which a succeeding age strove to complete.

During the period of iatro-chemistry, which may be

said to have extended from the first quarter of the sixteenth century to the latter half of the seventeenth, chemistry was advanced along practical lines by the labours of many men, chief of whom were Agricola the metallurgist, Palissy the potter, and Glauber the technologist. These men were primarily experimental chemists, who took little or no part in the fruitless polemics of the period, but followed their avocation in the true spirit of investigators, and thereby enriched science with many new and well-ascertained facts.

**George Agricola**, born at Glauchau in Saxony in 1494, was a contemporary of Paracelsus. After studying medicine at Leipzig, he devoted himself to metallurgy and mineralogy, first at Joachimsthal, and published a number of works which were long deservedly regarded as the leading treatises on these subjects.

In his *Libri XII. de re Metallica* he gives an account of what was known in his time respecting the extraction, preparation, and testing of ores. He describes the smelting of copper and the recovery of the silver which might be associated with it. He also describes methods of obtaining quicksilver, and of purifying it by treatment with salt and vinegar. He gives a full description of the method of obtaining gold by amalgamation, and of recovering the mercury by distillation. He gives accounts of the smelting of lead, tin, iron, bismuth, and antimony, and describes the manufacture of salt, nitre, alum, and green vitriol.

The whole work, which is of folio size, is illustrated by wood-cuts, which give a faithful idea of the nature of the several operations, and of the character of furnaces, trompes, bellows, and tools employed in them. It is by far the most important technical work of the sixteenth century, and it exercised great influence on the

art of metallurgy. The descriptions—at least as regards European processes—are evidently the result of personal observation. Agricola visited the mines, and faithfully noted the different methods of sorting and washing the ores, the characters of which he accurately describes. His accounts of the various smelting operations are so detailed that it is obvious they must have been put together after personal inquiry. The study of metallurgy, indeed, was the main object of his life; and he devoted to its pursuit even the pension which had been settled on him by Maurice, Elector of Saxony. He became Mayor of Chemnitz, died there in 1555, and was buried at Zeitz.

**Bernard Palissy** lived throughout the greater portion of the sixteenth century. Although not a professed chemist, nor a follower of any particular school, he was an ardent self-taught experimentalist and a keen and accurate observer, who greatly enriched ceramic art by his discoveries.

**Johann Rudolf Glauber** was born at Karlstadt, in Bavaria, in 1604, and after a restless life died in Amsterdam in his sixty-fourth year. He published an encyclopædia of chemical processes, in which he describes the preparation of a great variety of substances of technical importance. The greater number of the pharmacopœias of the seventeenth century are indebted to him for their descriptions of the mode of manufacture of their official preparations. He discovered sodium sulphate—his *sal mirabile*, still frequently named after him—and introduced it into medicine.

During this period the common mineral acids—sulphuric, hydrochloric, and nitric—became ordinary articles of commerce, and were used in the manufacture

of a number of useful products, chiefly inorganic salts. A considerable number of metallic oxides were also in common use, and were applied to a variety of purposes in the arts. The knowledge of definite organic substances was much more limited. Acetic acid had long been known, but was first obtained in a concentrated form during this period by the distillation of verdigris. A number of other acetates were also known, as well as certain tartrates—as, for example, salt of sorrel, Rochelle or seignette salt, and tartar emetic. Succinic and benzoic acid were introduced into medicine, and Tachenius discovered one of the characteristic acids of fat and oil (stearic acid). Spirit of wine was, of course, largely made and used in the preparation of tinctures and essences. Ether, originally known as *oleum vitrioli dulce verum*, was first discovered by Valerius Cordus ; and a mixture of it with alcohol, long known as Hoffmann's drops, appears to have been employed as a medicine by Paracelsus.

## CHAPTER VI.

### "THE SCEPTICAL CHEMIST": THE DAWN OF SCIENTIFIC CHEMISTRY

THE latter half of the seventeenth century was a remarkable period in the history of the intellectual development of Europe. At that time nearly every department of human knowledge seemed to have become permeated by an eager spirit of scepticism, inquiry, and reform. The foundation of the Royal Society of London for Improving Natural Knowledge, the Accademia del Cimento of Florence, the Academie Royale at Paris, the Berlin Academy, all within a few years of each other, was significant of the times. Chemistry was no longer to be a sacred mystery, to be known only to priests, and its secrets jealously guarded by them. Science had chafed under the domination of the schoolmen; it was now contemptuous of the dialectics of the Spagyrist. Experimentarian philosophy became even fashionable; and the purely deductive methods of the Peripatetics gradually gave place to the only sound method of advancing natural knowledge. The supremacy of the old philosophy may be said to have been first distinctly challenged by Robert Boyle. The appearance in 1661 of his book, *The Sceptical Chemist*, marks a turning-point in the history of chemistry. The "Chemico-physical Doubts and Paradoxes" raised by Boyle "touching the experiments whereby vulgar Spagyrist are wont to endeavour to evince their Salt, Sulphur, and Mercury to be the true Principles of Things,"

eventually sealed the fate of the doctrine of the *tria prima*, and of the tenets of the school of Paracelsus.

In this treatise Boyle sets out to prove that the number of the peripatetic elements or principles hitherto assumed by chemists is, to say the least, doubtful. The words "element" and "principle" are used by him as equivalent terms, and signify those primitive and simple bodies of which compounds may be said to be composed, and into which these compounds are ultimately resolvable. He considered that the matter of all bodies was originally divided into small particles of different shapes and sizes, and that these particles might unite into small "parcels," not easily separable again; that a great variety of compounds may arise from a few ingredients; that various substances are obtainable from bodies by fire; that fire is not the true and genuine analyser of bodies, since it does not separate the principles of a body, but variously alters its nature; and that some things obtained from a body by fire were not its proper or essential ingredients. Three is not precisely and universally the number of the distinct substances or elements into which all compound bodies are resolvable by fire, inasmuch as some bodies afford more than three principles. Earth and water are as much chemical principles as salt, sulphur, and mercury. Even the limitation to five chemical principles is too narrow. Such is proved to be the case by the mode in which bodies, animal and vegetable, grow, and by the analysis of minerals and metals. The chemical theory of "qualities" of the Spagyrist is narrow, defective, and uncertain; supposes things not proved; is often superfluous, and frequently contradicts the phenomena of nature. The "principles" found in bodies cannot be the cause of their qualities, since contrary qualities



are ascribed to the same body. He concludes, therefore, that the Paracelsian elements — their "salt," "sulphur," and "mercury"—are not the first and most simple principles of bodies; but that these consist, at most, of concretions of corpuscles or particles more simple than they, and possessing the radical and universal properties of volume, shape, and motion.

**Robert Boyle**, fourteenth child and the seventh and youngest son of Richard the "Great" Earl of Cork, and Lord High Chancellor of Ireland, was born at Lismore in 1626. He was educated at Eton under Sir Henry Wotton, and, after spending some years on the Continent, settled at Stalbridge in Dorset, where he owned a manor. He became a member of what was known as the Invisible College, a small association of men interested in the new philosophy, who met at each other's houses in London, and occasionally at Gresham College, "to discourse and consider of philosophical inquiries and such as related thereunto." The meetings were subsequently held in Oxford, and Boyle took up his residence there in 1654. Here—in association with Wilkins; John Wallis and Seth Ward, the two Savilian Professors of Geometry and Astronomy; Thomas Willis, the physician, then student of Christ Church; Christopher Wren, then Fellow of All Souls' College; Goddard, Warden of Merton; and Ralph Bathurst, Fellow of Trinity, and afterwards its President—they sought to cultivate the new philosophy, "being satisfied that there was no certain way of arriving at any competent knowledge unless they made a variety of experiments upon natural bodies. In order to discover what phenomena they would produce, they pursued that method by themselves with great industry, and then communicated their discoveries to each other." The



ROBERT BOYLE.

From a painting by F. Kerseboom in the possession of the Royal Society.

Invisible College eventually grew into the Royal Society, which received its charter in 1663. Boyle removed to London in 1668, and died there on December 31st, 1691, in the sixty-fifth year of his age.

A man of integrity, modest, simple, and unassuming, Boyle was an assiduous and true student of science, and practically the whole of his life was given to its pursuit. His social position, his example, the purity of his private life, and the fame of his discoveries made his personal influence very considerable, to the great advantage of science in this country. His experimental work was of a high order. He introduced the air-pump into England, and his "pneumatical engine" enabled him to discover many of the fundamental properties of a gas, notably the relation of its volume to pressure. He also discovered the dependence of the boiling point of a liquid upon atmospheric pressure, explained the action of the syphon, the effect of the air on the vibration of a pendulum and on the propagation of sound, and made experiments on the nature of flame, and on the relation of air to combustion and respiration. In his *History of Fluidity* he seeks to show that a body seems to be fluid by consisting of corpuscles touching one another only in some parts of their surfaces; whence, by reason of the numerous spaces between them, they easily glide along each other till they meet with some resisting body to whose internal surface they exquisitely accommodate themselves. He considers the requisites of fluidity to be chiefly these: The smallness of the component particles, their determinate figure, the vacant spaces between them, and the fact of their being agitated variously and apart by their own innate motion or by some thinner substance which tosses them about in its

passage through them. His published works contain many well-authenticated chemical facts, which are commonly held to be the discovery of a later time. He prepared acetone by the distillation of the acetates of lead and lime ; and he isolated methyl alcohol from the products of the destructive distillation of wood. He was one of the earliest to insist on the necessity of studying the forms of crystals. He saw in their formation proof that the internal motions, configuration, and position of the integral parts are all that is necessary to account for alterations and diversities in outward character. Some of the stock illustrations of our lecture-rooms were of his contrivance. Thus he illustrated the expansive power of freezing water by bursting a plugged gun-barrel filled with water by solidifying the water by means of a mixture of snow and salt—a freezing mixture which he first introduced.

Boyle was the first to formulate our present conception of an element in contradistinction to that of the Greeks and the schoolmen who influenced the theories of the iatro-chemists. In the sense understood by him, the Aristotelian elements were not true elements, nor were the salt, sulphur, and mercury of the school of Paracelsus. He was also the first to define the relation of an element to a compound, and to draw the distinction we still make between compounds and mixtures. He revived the atomic hypothesis, and explained chemical combination on the basis of affinity. He contended that one of the main objects of the chemist was to ascertain the nature of compounds ; and thereby he stimulated the application of analysis to chemistry. Boyle discovered a number of qualitative reactions, and applied them to the detection of substances, either free or in combination

But Boyle's greatest service to learning consisted in the new spirit he introduced into chemistry. Henceforward chemistry was no longer the mere helpmeet of medicine. She became an independent science, the principles of which were to be ascertained by experiment; a science to be studied with the object of discovering the laws regulating the phenomena with which it is concerned—and hence elucidating truth for truth's sake. The old philosophy of the Greeks had, as we have seen, become merged into the doctrine of the iatro-chemists; and this was now to be purified from the theosophical mysticism with which Paracelsus and his followers had enshrouded it. "The dialectical subtleties of the schoolmen much more," says Boyle, "declare the wit of him that uses them than increase the knowledge or remove the doubts of sober lovers of truth.....For in such speculative inquiries where the naked knowledge of the truth is the thing principally aimed at, what does he teach me worth thanks, that does not, if he can, make his notion intelligible to me, but by mystical terms and ambiguous phrases darkens what he should clear up, and makes me add the trouble of guessing at the sense of what he equivocally expresses, to that of learning the truth of what he seems to deliver." The influence of the new spirit thus infused into the science by Boyle is seen in the general style of chemical literature at the end of the seventeenth century, when compared with that of the close of the sixteenth. The mysticism and obscurity of the alchemists were no longer tolerated.

Boyle was slender and tall, with a countenance pale and emaciated. His constitution was delicate and his body feeble, and it was only by strict attention to diet and regularity of exercise that he accomplished

what he did. Although he suffered occasionally from an excessive lowness of spirits, there was nothing morose or ascetic in his nature. He was never married, although, says his friend John Evelyn, "few men were more facetious and agreeable in conversation with the ladies whenever he happened to be engaged among them."

Kindly, courteous, charitable; unaffected, and temperate in his manner of life, Boyle enjoyed the respect and esteem of all his contemporaries. It was said of him that he was never known to have offended any person in his whole life by any part of his deportment. He allowed himself a great deal of decent cheerfulness, and had about him all the tenderness of good nature, as well as all the softness of friendship. These gave him a large share of other men's concerns, for he had a quick sense of the miseries of mankind. Although a philosopher in the broadest sense of that term, his peculiar and favourite study was chemistry, "in which," says Bishop Burnet, "he engaged with none of those ravenous and ambitious designs that drew many into them. His design was only to find out nature, to see into what principles things might be resolved, and of what they were compounded."

**John Kunkel**, born in 1630, was the son of an alchemist attached to the Court of the Duke of Holstein. After serving his father for some years, he obtained employment as chemist and pharmacist under the Dukes Charles and Henry, of Lauenburg. He subsequently entered the laboratory at Dresden of John George II., Elector of Saxony, and, after teaching chemistry at the University of Wittenburg, then famous as a medical school, he accepted an invitation to take charge of the glass works and laboratory of the Elector of Brandenburg, at Berlin. The laboratory was burnt down, and

then Charles XI. of Sweden called him to Stockholm and ennobled him as Baron von Lowenstiern. He died in Stockholm in 1702. Kunkel's chief work is his *Laboratorium Chymicum*, published after his death. It was written in German. In it Kunkel relates how he acquired possession of a knowledge of the manufacture of Baldwin's phosphorus, and of the phosphorus discovered by Brand—perhaps the most important, as it certainly was one of the most striking, of the chemical discoveries of the seventeenth century.

Kunkel did much to liberate chemical literature from the mysticism and obscurity of alchemy. He was scornful of the theories of the adepts, and contemptuous of their *tria prima*.

I, old man that I am, who have been occupied with chemistry for sixty years, have never yet been able to discover their fixed sulphur, or how it enters into the composition of metals.....Moreover, they are not agreed among themselves respecting the kind of sulphur. The sulphur of one is not the sulphur of the other. To that one may reply that each is at liberty to baptise his child as he likes. I agree: you may even, if you are so disposed, call an ass a cow; but you will never make anyone believe that your cow is an ass.

As to the alkahest he says:—

There has been much discussion concerning this grand natural solvent. Some derive it from the Latin—*alkali est*; others from the two German words *all geist* (all gas); lastly, others say it is from *alles est* (that's all). As to myself, I do not believe in Van Helmont's universal solvent. I call it by its true name—*alles Lügen heist*, or *alles Lügen ist* (it is all a lie).

Kunkel discovered the secret of the manufacture of aventurine glass and of ruby glass by means of the purple of Cassius—a product from gold first obtained

by a doctor of medicine of that name in Hamburg. He made observations on fermentation and putrefaction—recognised that alum was a double salt (*sal duplicatum*); described the present method of preparing pure silver, and of parting gold and silver by means of sulphuric acid. He also described the mode of preparing a number of essential oils, detected the presence of stearopten in oils, and discovered nitrous ether.

**John Joachim Becher**, the son of a Lutheran minister, was born at Speyer in 1635. Owing to the death of his father and the devastation of the family property during the Thirty Years' War, Becher had a hard struggle with poverty during his youth, and led a restless, wandering life. In 1666 he was Professor of Medicine in the University of Mayence. Subsequently he went to Munich as head of the finest laboratory in Europe, but, quarrelling with the Chancellor of the Bavarian Court, betook himself to Vienna. After a short stay there, he quitted Austria for Holland, and established himself in Haarlem. Here he proposed to the States-General to extract gold from the sand-dunes; but, the project failing, he left for England and visited the Cornish mines. On the invitation of the Duke of Mecklenburg-Güstrow, he returned to Germany. Shortly afterwards (in 1682) he died, in the forty-seventh year of his age. Becher's name is remembered mainly in connection with his theory of combustion, which, as we shall see, was subsequently developed by Stahl into the theory of Phlogiston—a generalisation which dominated chemistry until near the close of the eighteenth century.

**John Mayow**, born in Cornwall in 1645, was a practising physician, whose name chiefly lives by virtue of his clear recognition of the substance or principle in the air which is concerned in combustion, the calcination of



metals, respiration, and the conversion of venous into arterial blood. This substance, which he found to be contained in saltpetre, he called *spiritus igno-aëreus* or *nitro aëreus*. Mayow died at the age of thirty-four. Had he been able to follow up his observations, he might have influenced very materially the development of theoretical chemistry. As it was, he was practically overlooked by his contemporaries, and the real significance of his work was not appreciated until long afterwards.

**Nicolas Lemery**, also born in 1645, wrote a *Cours de Chimie*, one of the best text-books of the time, which passed through as many as thirteen editions, and was translated into English, German, Latin, Italian, and Spanish.

In this book he strove, as he says, to express himself clearly, and to avoid the obscurities which were to be found in the authors who had preceded him.

The fine imaginations of other philosophers concerning their physical principles may elevate the spirit by their grand ideas, but they prove nothing demonstratively. And, as chemistry is a science of observation, it can only be based on what is palpable and demonstrative.

Nicolas Lemery, who is not to be confounded with his son Louis, also a chemist, made a considerable number of contributions to pharmaceutical chemistry; and his *Pharmacopée Universelle*, *Dictionnaire Universel des Drogues Simples*, and *Traité de l'Antimoine* were standard works in their day.

Lemery was at one time a Protestant, and on the revocation of the Edict of Nantes fled to England; but, embracing Catholicism, he returned to Paris, re-established his pharmacy, and was elected into the Academy in 1699. He died in 1715.

**William Homberg**, born in Batavia in 1652, was originally intended for the profession of law, but, becoming attached to science, studied botany and medicine in Padua, chemistry at Bologna and in London, mechanics and optics at Rome, and anatomy at Leyden. In the course of his travels he visited the mines of Germany, Hungary, Bohemia, and Sweden. In 1682 he was invited to Paris by Colbert, and in 1691 was made a member of the Academy and was placed by the Duke of Orleans in charge of his laboratory—then one of the finest in Europe. Homberg married the daughter of Dodart, the physician. She became an expert *préparateur*, and was of great assistance to him in his experimental inquiries. He first made known the existence of phosphorus in France, discovered by Brand, of Hamburg, and he described the phosphorescent salt associated with his name. He made important observations on the saturation of alkalis by acids, and was aware that they combined in different proportions. He was an industrious worker, and, with the exception of Cassini, was the most active member of the Academy. He died on September 24th, 1715.

Next to Boyle,\* perhaps the most active agent in emancipating chemistry from the yoke of alchemy was Boerhaave, who, by his teaching as Professor of Physic, raised the University of Leyden to the summit of its fame.

**Hermann Boerhaave**, the son of a minister, was born near Leyden, in 1668. He occupied himself in turn with theology, classics, mathematics, chemistry, and botany, when he turned to physic, and, after a course of study at the University of Harderwyk, in Gelderland, began to practise. In 1702 he was appointed to a lectureship, and eventually to the Chair of Medicine,



After a painting by T. Wandelaar.

in the University of Leyden, of which he became Rector in 1714. His reputation as a teacher spread throughout Europe, and steadily increased until his death.

Boerhaave was one of the most learned men of his age, and singularly well cultured, not only in science, but in history, poetry, and polite literature. He conversed in English, French, and German, and read Italian and Spanish with facility. "The Latin he spoke extempore in lectures or conversation was so clear that, with his action, method, and the aptness of his similes, he could level the most abstruse points to the meanest capacities."<sup>1</sup> He was fond of music, and a good performer on several instruments, particularly the lute. He delighted to welcome musicians to his house. His profession as a physician brought him wealth, much of which he spent in horticulture; and the garden of his country seat, nearly eight acres in extent, was enriched with all the exotic trees he could procure and induce to flourish in the climate of Holland.

Boerhaave was of a robust frame and healthy constitution, early inured to constant exercise and the inclemencies of weather. His stature was rather tall, and his habit corpulent. "He had a large head, short neck, florid complexion, light brown curled hair (for he did not wear a wig), an open countenance, and resembled Socrates in the flatness of his nose and his natural urbanity."<sup>2</sup> He died at Leyden on September 23rd, 1738, in the seventieth year of his age.

As a chemist Boerhaave is chiefly known by his *Elementa Chymia*, published in 1732—the most complete and most luminous chemical treatise of its time, translations of which appeared in the chief European languages.

<sup>1</sup> Burton, *Life of Boerhaave*, p. 58 *et seq.*

<sup>2</sup> *Ibid.*

The work is divided into three main parts. The first is concerned with the origin and progress of the art, and with the personal history of its most distinguished cultivators. The second and largest part deals with the attempt to form a system of chemistry based on such observational matter as seemed well established. The third consists of a collection of chemical processes relating to the analysis or decomposition of bodies, grouped under the heads of "vegetables," "animals," and "fossils"—the beginnings, in fact, of a sub-division of the science into organic and inorganic chemistry.

As regards his belief in alchemy, Boerhaave was an agnostic: he neither affirmed nor denied the possibility of transmutation. In this respect he resembled Newton and Boyle. Boyle, indeed, was singularly cautious and reticent in his references to alchemistic matters. As was said of him by Shaw, he was too wise to set any bounds to nature: he was not prone to say that every strange thing must needs be impossible, for he saw strange things every day, and was well aware that there are powerful forces in the world of whose laws and modes of action he knew nothing. With that wariness which was habitual to him, he was wont to say that "those who had seen them might better believe them than those who had not"; and he was modest enough to suppose that Paracelsus or Helmont might conceivably know of agents of which he was ignorant.

Boerhaave unquestionably spent much time in the study of alchemical works, particularly those of Paracelsus and Helmont, which he repeatedly read. The *Philosophical Transactions* of the Royal Society contain the results of a laborious but fruitless investigation by him on quicksilver, which he undertook in the hope of discovering the seminal or engendering matter which,

on the old theory of the generation of metals, was supposed to be contained in mercury. But although, as he relates, he tortured it by "conquassation, trituration, digestion, and by distillation, either alone or amalgamated with lead, tin, or gold, repeating this operation to 511 or even to 877 distillations," the mercury appeared only "rather more bright and liquid, without any other variation in its form or virtues, and acquired very little, if any, increase of its specific gravity."

**Stephen Hales** (1677-1761), an ingenious divine—he held the perpetual curacy of Teddington, and lived practically the greater part of his life there—distinguished as a physiologist and inventor, occupied himself in chemical pursuits, and made a number of observations on the production of gaseous substances. His results were communicated to the Royal Society and subsequently republished, in a collected form, under the title of *Statical Essays*. In these experiments he used methods very similar in principle to those subsequently employed by Priestley. It is evident from his description of his experiments that he must have prepared a considerable number of gaseous substances—hydrogen, carbonic acid, carbonic oxide, sulphur dioxide, marsh gas, etc.—but he seems to have made no systematic attempt to study their properties, as he considered that they were simply air, modified or "tinctured" by the presence of substances which he regarded as more or less fortuitous. Prior to the time of Black all forms of gaseous substance were regarded as substantially identical—in fact, as being *air*, as understood by the Ancients—a simple elementary substance. It was Black's study of carbonic acid which first clearly established that there were essentially distinct varieties of gaseous matter.

## CHAPTER VII.

### PHLOGISTONISM

EVEN before the appearance of *The Sceptical Chemist* there was a growing conviction that the old hypotheses as to the essential nature of matter were inadequate and misleading. We have seen how the four "elements" of the Peripatetics had become merged into the *tria prima*—the "salt," "sulphur," and "mercury"—of the Paracelsians. As the phenomena of chemical action became better known, the later iatro-chemists—or, rather, that section of them which recognised that chemistry had wider aims than to minister merely to medicine—felt that the conception of the *tria prima*, as understood by Paracelsus and his followers, was incapable of being generalised into a theory of chemistry. Beche., while clinging to the conception of three primordial substances as making up all forms of matter, changed the qualities hitherto associated with them. According to the new theory, all matter was composed of a mercurial, a vitreous, and a combustible substance or principle, in varying proportions, depending upon the nature of the particular form of matter. When a body was burnt or a metal calcined, the combustible substance—the *terra pinguis* of Becher—escaped.

This attempt to connect the phenomena of combustion and calcination with the general phenomena of chemistry was still further developed by Stahl, and was eventually extended into a comprehensive theory of chemistry, which was fairly satisfactory so long as

no effort was made to test its sufficiency by an appeal to the balance.

**George Ernest Stahl**, who developed Becher's notion into the theory of *phlogiston* (φλογιστός—burnt), and thereby created a generalisation which first made chemistry a science, was born at Anspach in 1660, became Professor of Medicine and Chemistry at Halle in 1693, physician to the King of Prussia in 1716, and died in Berlin in 1734.

Stahl contributed little or nothing to practical chemistry; and no new fact or discovery is associated with his name. His service to science consists in the temporary success he achieved in grouping chemical phenomena, and in explaining them consistently by a comprehensive hypothesis.

The theory of phlogiston was originally broached as a theory of combustion. According to this theory, bodies such as coal, charcoal, wood, oil, fat, etc., burn because they contain a combustible principle, which was assumed to be a material substance and uniform in character. This substance was known as phlogiston. All combustible bodies were to be regarded, therefore, as compounds, one of their constituents being phlogiston: their different natures depended partly upon the proportion of phlogiston they contain, and partly upon the nature and amount of their other constituents. A body, when burning, was parting with its phlogiston; and all the phenomena of combustion—the flame, heat, and light—were caused by the violence of the expulsion of that substance. Certain metals—as, for example, zinc—could be caused to burn, and thereby to yield earthy substances, sometimes white in colour, at other times variously coloured. These earthy substances were called *calces*, from their general resemblance to lime.



Other metals, like lead and mercury, did not appear to burn; but on heating them they gradually lost their metallic appearance, and became converted into calces. This operation was known as calcination. In the act of burning or of calcination phlogiston was expelled. Hence metals were essentially compound: they consisted of phlogiston and a calx, the nature of which determined the character of the metal. By adding phlogiston to a calx the metal was regenerated. Thus, on heating the calx of zinc or of lead with coal, or charcoal, or wood, metallic zinc or lead was again formed. When a candle burns, its phlogiston is transferred to the air; if burned in a limited supply of air, combustion ceases, because the air becomes saturated with phlogiston.

Respiration is a kind of combustion whereby the temperature of the body is maintained. It consists simply in the transference of the phlogiston of the body to the air. If we attempt to breathe in a confined space, the air becomes eventually saturated with the phlogiston, and respiration stops. The various manifestations of chemical action, in like manner, were attributed to this passing to and fro of phlogiston. The colour of a substance is connected with the amount of phlogiston it contains. Thus, when lead is heated, it yields a yellow substance (litharge); when still further heated, it yields a red substance (red lead). These differences in colour were supposed to depend upon the varying amount of phlogiston expelled.

The doctrine of phlogiston was embraced by nearly all Stahl's German contemporaries, notably by Marggraf, Neumann, Eller, and Pott. It spread into Sweden, and was accepted by Bergman and Scheele; into France, where it was taught by Duhamel, Rouelle, and Macquer; and into Great Britain, where its most

influential supporters were Priestley and Cavendish. It continued to be the orthodox faith until the last quarter of the eighteenth century, when, after the discovery of oxygen, it was overturned by Lavoisier.

During the sway of phlogiston chemistry many notable advances—not by its aid, but rather in spite of it. At a matter of fact, until the time of Lavoisier few if any investigations were made with the express intention of testing it, or of establishing its sufficiency. When new phenomena were observed the attempt was no doubt made to explain them by its aid, frequently with no satisfactory result. Indeed, even in the time of Stahl facts were known which it was difficult or impossible to reconcile with his doctrine; but these were either ignored, or their true import explained away. Although, therefore, these advances were in no way connected with phlogiston, it will be convenient to deal with the more important of them now, inasmuch as they were made during the phlogistic period.

With the exception of Marggraf, Stahl's German contemporaries contributed few facts of first-rate importance to chemistry. **Pott**, who was born at Halberstadt in 1692 and became Professor of Chemistry in Berlin in 1737, is chiefly remembered by his work on porcelain, the chemical nature and mode of origin of which he first elucidated. **Marggraf**, born in Berlin in 1709, was one of the best analysts of his age. He first clearly distinguished between lime and alumina, and was one of the earliest to point out that the vegetable alkali (potash) differed from the mineral alkali (soda). He also showed that gypsum, heavy spar, and potassium sulphate were analogous in composition. He clearly indicated the relation of phosphoric acid to phosphorus, described a number of methods of preparing that acid,

and explained the origin of the phosphoric acid in urine.

Of the Swedish chemists of that period, the most notable was Scheele.



CARL WILHELM SCHEELE.

From the statue by Börjeson at Stockholm.

**Carl Wilhelm Scheele** was born in 1742 at Stralsund. When fourteen years of age he was apprenticed to an apothecary at Gothenburg, and began the study of experimental chemistry, which he continued to prosecute

as an apothecary at Malmö, Stockholm, Upsala, and eventually at Köping on Lake Malar, where he died in 1786, in the forty-third year of his age. During the comparatively short period of his scientific activity Scheele made himself the greatest chemical discoverer of his time.

He first isolated chlorine, and determined the individuality of manganese and baryta. He was an independent discoverer of oxygen, ammonia, and hydrogen chloride. He discovered also hydrofluoric, nitro-sulphonic, molybdic, tungstic, and arsenic, among the inorganic acids; and lactic, gallic, pyrogallie, oxalic, citric, tartaric, malic, mucic, and uric acids among the organic acids. He isolated glycerine and milk-sugar; determined the nature of microcosmic salt, borax, and Prussian blue, and prepared hydrocyanic acid. He demonstrated that graphite is a form of carbon. He discovered the chemical nature of sulphuretted hydrogen, arsenuretted hydrogen, and the green arsenical pigment known by his name. He invented new processes for preparing ether, powder of algaroth, phosphorus, calomel, and *magnesia alba*. He first prepared ferrous ammonium sulphate; showed how iron may be analytically separated from manganese; and described the method of breaking up mineral silicates by fusion with alkaline carbonates. Scheele's contributions to chemical theory were slight and unimportant, but as a discoverer he stands pre-eminent.

Of the French phlogistians we have space only to mention Duhamel and Macquer.

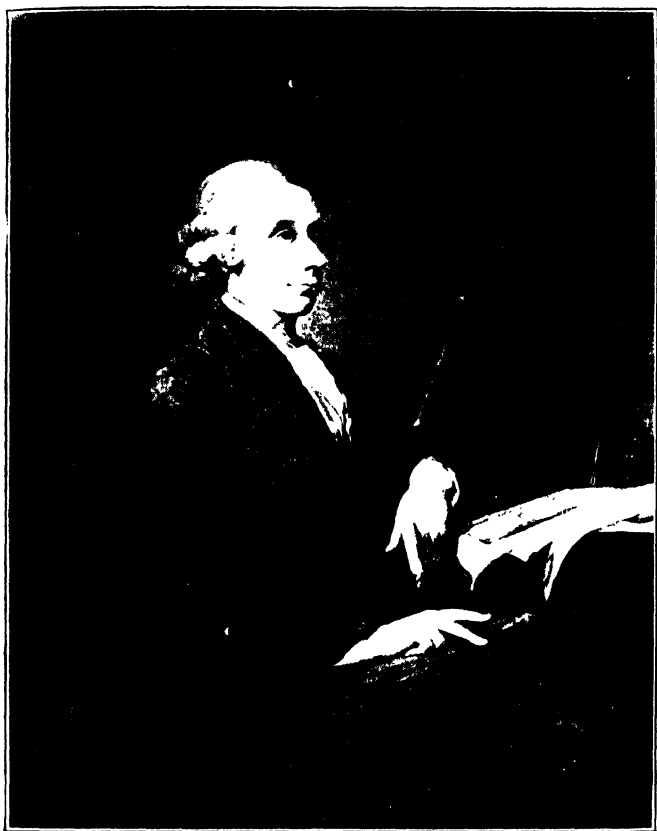
**Henry Louis Duhamel du Monceau** was born at Paris in 1700. He was one of the earliest to make experiments on ossification, and one of the first to detect the difference between potash and soda.

**Peter Joseph Macquer** was born in 1718 at Paris. He investigated the nature of Prussian blue (discovered by Diesbach, of Berlin, in 1710), worked on platinum, wrote one of the best text-books of his time, published a dictionary of chemistry, and was an authority on the chemistry of dyeing.

In addition to those already mentioned, the most notable names as workers in chemistry in Great Britain during the eighteenth century are Black, Priestley, and Cavendish.

**Joseph Black** was born in 1728 at Bordeaux, where his father was engaged in the wine trade. A student of the University of Glasgow, he became its Professor of Chemistry in 1756. In 1766 he was transferred to the Chemical Chair of the University of Edinburgh, and died in 1799. Black published only three papers, the most important of which is entitled *Experiments upon Magnesia Alba, Quicklime, and Other Alkaline Substances*. He proved that magnesia is a peculiar earth differing in properties from lime. Lime is a pure earth, while limestone is carbonate of lime. He showed that magnesia will also combine with carbonic acid, and he explained that the difference between the mild and caustic alkalis is that the former contain carbonic acid, whereas the latter do not. He also explained how lime is able to convert the mild alkalis into caustic alkalis. Simple and well known as these facts are to-day, their discovery in 1755 excited great interest, and marked an epoch in the history of chemistry. Black's name is associated with the discovery of latent and specific heat, and he made the first determinations of the amount of heat required to convert ice into water.

**Joseph Priestley**, the son of a clothdresser, was born in 1733 at Fieldhead, near Leeds. When seven years



JOSEPH PRIESTLEY.

*From a mezzotint after Fuseli in the possession of the Royal Society.*

of age, on the death of his mother, he was taken charge of by his aunt, and was educated for the Nonconformist ministry, eventually becoming a Unitarian. He was first attracted to science by the study of electricity, of which he compiled a history. At Leeds, where he had charge of the Mill Hill congregation, he turned his attention to chemistry, mainly from the circumstance that he lived near a brewery and had the opportunity of procuring large quantities of carbonic acid, the properties of which he carefully studied. He abandoned the ministry for a time to become librarian and literary companion to Lord Shelburne, with whom he remained seven years. During this time he industriously pursued chemical inquiry, and discovered a large number of æriform bodies—viz., nitric oxide, hydrogen chloride, sulphur dioxide, silicon fluoride, ammonia, nitrous oxide, and, most important of all from the point of view of chemical theory, oxygen gas. Priestley's work gave a remarkable impetus to the study of pneumatic chemistry. It exercised great influence on the extension of chemical science, and—in other hands than his—on the development of chemical theory. The most important of his contributions to science are contained in his *Experiments and Observations on Different Kinds of Air*. This work not only gives an account of the methods by which he isolated the gases he discovered, but describes a great number of incidental observations, such as the action of vegetation on respired air, showing that the green parts of plants are able in sunlight to decompose carbonic acid and to restore oxygen to the atmosphere. He was, in fact, one of the earliest to trace the specific action of animals and plants on atmospheric air, and to show how these specific actions maintained its purity and constancy of

composition. He initiated the art of eudiometry (gas analysis), and was the first to establish that the air is not a simple substance, as imagined by the ancients. Priestley is to be credited with the invention of *soda-water*, which he prepared as a remedy for scurvy; and his name is connected with the so-called *pneumatic trough*—a simple enough piece of apparatus, but one which proved to be of the greatest service to him in his inquiries.

After leaving Lord Shelburne, Priestley removed to Birmingham and resumed his ministry. His religious and political opinions made him obnoxious to the Church and State party; and during the riots of 1791 his house was wrecked, his books and apparatus destroyed, and his life endangered. Eventually he emigrated to America, and settled at Northumberland, where he died on February 6th, 1804, in the seventy-first year of his age.

**Henry Cavendish** was born at Nice in 1731, and died in London in 1810. He was a natural philosopher in the widest sense of that term, and occupied himself in turn with nearly every branch of physical science. He was a capable astronomer, and an excellent mathematician, and he was one of the earliest to work on the subject of specific heat, and to improve the thermometer and the methods of making thermometric observations. He also determined the mean density of the earth. He made accurate observations on the properties of carbonic acid and hydrogen, greatly improved the methods of eudiometry, and first established the practical uniformity of the composition of atmospheric air. His greatest discovery, however, was his determination of *the composition of water*. He was the first to prove that water is not a simple or elementary substance, as supposed





From a drawing by Alexander in the Print Room of the British Museum.

by the ancients, but is a compound of hydrogen and oxygen. In certain of his trials he found that the water formed by the union of oxygen and hydrogen was acid to the taste ; and the search for the cause of this acidity led him to the discovery of the *composition of nitric acid*. He was the first to make a fairly accurate analysis of a natural water, and to explain what is known as the *hardness of water*.

Phlogistonism may be said to have dominated chemistry during three-fourths of the eighteenth century. Although radically false as a conception and of little use in the true interpretation of chemical phenomena, it cannot be said to have actually retarded the pursuit of chemistry. Men went on working and accumulating chemical facts uninspired and, for the most part, uninfluenced by it. Even Priestley, perhaps one of the most conservative of the followers of Stahl, regarded his dogma with a complacent tolerance ; and as its inconsistencies became apparent he was more than once on the point of renouncing it. Of one thing he was quite convinced, and that was that Stahl had greatly erred in his conception of the real nature of phlogiston. Perhaps the most signal disservice which phlogiston did to chemistry was to delay the general recognition of Boyle's views of the nature of the elements. The alchemists, it will be remembered, regarded the metals as essentially compound. Boyle was disposed to believe that they were simple. Becher and Stahl and their followers, until the last quarter of the eighteenth century, also regarded them as compounds, phlogiston being one of their constituents. On the other hand, what we now know to be compounds—such as the calces, the acids, and water itself—were held by the phlogistians to be simple substances.

The discovery, in 1774, of oxygen—the dephlogisticated air of Priestley—and the recognition of the part it plays in the phenomena which phlogiston was invoked to explain, mark the termination of one era in chemical history and the beginning of another. Before entering upon an account of the new era it is desirable to take stock of the actual condition of chemical knowledge at the end of the phlogistic period, and to show what advances had been made in pure and applied chemistry during that time.

During the eighteenth century greater insight was gained into the operations of the form of energy with which chemistry is mainly concerned, and views concerning chemical affinity and its causes began to assume more definite shape, chiefly owing to the labours of Boerhaave, Bergman, Geoffroy, and Rouelle. It was clearly recognised that the large group of substances comprised under the term “salts” were compound, and made up of two contrasted and, in a sense, antagonistic constituents, classed generically as acids and bases.

On the practical side chemistry made considerable progress. Analysis—a term originally applied by Boyle—greatly advanced. It was, of course, mainly qualitative; but, thanks to the labours of Boyle, Hoffmann, Marggraf, Scheele, Bergman, Gahn, and Cronstedt, certain reactions and reagents came to be systematically applied to the recognition of chemical substances, and the precision with which these reagents were used led to the detection of hitherto unknown elements. The beginnings of a quantitative analysis were made even before the time of Boyle, but its principles were greatly developed by him, and were further extended by Homborg, Marggraf, and Bergman. Marggraf accurately determined the amount of silver chloride

formed by adding common salt to a solution of a known weight of silver, and Bergman first pointed out that estimations of substances might be conveniently made by weighing them in the form of suitably prepared compounds, which, it was implicitly assumed, were of uniform and constant composition. The foundations of an accurate system of gaseous analysis were made by Cavendish; and various forms of physical apparatus were applied to the service of chemistry.

To the elements which were known prior to Boyle's time, although not recognised as such, there were added phosphorus (Brand, 1669), nitrogen (Rutherford), chlorine (Scheele, 1774), manganese (Gahn, 1774), cobalt (Brandt, 1742), nickel (Cronstedt, 1750), and platinum (Watson, 1750). Baryta was discovered by Scheele, and strontia by Crawford. Phosphoric acid was discovered by Boyle, and its true nature determined by Marggraf; Cavendish first made known the composition of nitric acid. As already stated, Scheele first isolated molybdic and tungstic acids and determined the existence of a number of the organic acids (p. 75). Other discoveries—such as the true nature of limestone and *magnesia alba* and their relations respectively to lime and magnesia by Black, the many gaseous substances by Priestley, and the compound nature of water by Cavendish—have already been referred to.

Technical chemistry also greatly developed during the eighteenth century, thanks to the efforts of Gahn, Marggraf, Duhamel, Reaumur, Macquer, Kunkel, and Hellot; and many important industrial processes—such as the manufacture of sulphuric acid by Ward of Richmond, and subsequently by Roebuck at Birmingham, and the Leblanc process of conversion of common salt into alkali—had their origin during this period.

## CHAPTER VIII.

### LAVOISIER AND LA RÉVOLUTION CHIMIQUE

WE have seen how chemistry made a new departure during the political upheaval which occurred in this country about the middle of the seventeenth century. It acquired a new impetus and took a fresh course during the political cataclysm which overwhelmed France and alarmed Europe towards the close of the eighteenth century. The instigator and leader of this second revolution in chemistry was Lavoisier, one of the most distinguished men of his age, and himself a victim of the political fury of his own people.

**Antoine-Laurent Lavoisier** was born in Paris in 1743. At the Jardin du Roi he came under the influence of Rouelle, one of the best teachers of his time, who eventually shaped his career as a chemist. In 1765 he sent to the Academy his first paper on gypsum, which is noteworthy as giving for the first time the true explanation of the "setting" of plaster of Paris, and the reason why overburnt gypsum will not rehydrate. Three years later he became a member of the *Ferme-général*—a company of financiers to whom the State conceded, for a fixed annual sum, the right of collecting the indirect taxes of the country. It was this connection that brought Lavoisier to the scaffold during the revolution of 1794. Like Stahl, Lavoisier discovered no new substance; but, also like Stahl, he created a new epoch by destroying the philosophical system which Stahl had established.

It is commonly stated that the exception is a proof of the rule. The history of science can show many instances whereby the rule has been demolished by the exception. Little facts have killed big theories, even as a pebble has slain a giant. During the reign of phlogiston a few of such facts were not unknown—at least to some of the better informed of Stahl's followers.

Some of the alchemists had discovered that a metal gained, not lost, weight by calcination. This was known as far back as the sixteenth century. It had been pointed out by Cardan and by Libavius. Sulzbach showed that such was the case with mercury. Boyle proved it in the case of tin, and Key in that of lead. Moreover, as knowledge increased it became certain that Stahl's original conception of the principle of combustion as a ponderable substance—he imagined, with Becher, that it was of the nature of an earth—was not tenable. The later phlogistians were disposed to regard it as probably identical with hydrogen. But even hydrogen has weight, and facts seemed to require that phlogiston, if it existed at all, should be devoid of weight.

Towards the latter half of the eighteenth century clearer views began to be held concerning the relations of atmospheric air to the phenomena of combustion and of calcination; many half-forgotten facts relating to these phenomena were recalled, and the inconsistencies and insufficiency of phlogiston as a dogma became gradually manifest. Three cardinal facts conspired to bring about its overthrow—the isolation of oxygen by Priestley; the recognition by him of the nature of atmospheric air, and of the fact that one of its constituents is oxygen; and, lastly, the discovery by Cavendish that water is a compound, and that its constituents are

oxygen and hydrogen. The significance of these facts was first clearly grasped by Lavoisier, and to him is due the credit of their true interpretation. By reasoning and experiment he proved conclusively that all ordinary phenomena of burning are so many instances of the combination of the oxygen of the air with the combustible substance; that calcination is a process of combination of the oxygen in the air with the metal, which thereby increases in weight by the amount of oxygen combined. Water—no longer a simple substance—is formed by the union, weight for weight, of oxygen and hydrogen. Lavoisier's reasoning was so sound and his experimental evidence so complete that his views gradually gained acceptance in France. The phlogiston myth was thus exploded. Inspired by Lavoisier, a small band of French chemists—Berthollet, Fourcroy, Guyton de Morveau—thereupon set to work to remodel the system of chemistry and to recast its nomenclature so as to eliminate all reference to phlogiston. The very names "oxygen," "hydrogen," "nitrogen," corresponding respectively to the "dephlogisticated air," "phlogiston," and "phlogisticated air" of Priestley, were coined by the new French school. For a time *le principe oxygène* was regarded by this school in much the same relation as phlogiston was regarded by Stahl and his followers. The one fetich was exchanged for the other. The combustible principle—phlogiston—was renounced for the acidifying principle—oxygen. The new chemistry for a time centred itself round oxygen, just as the old chemistry had centred itself round phlogiston. The views of the French school met with no immediate acceptance in Germany, the home of phlogistonism, or in Sweden or England, possibly owing, to some extent, to national prejudices. The

spirit of revolution, even although it might be an intellectual revolution, had not extended to these countries. Priestley, Cavendish, and Scheele could not be induced to accept the new doctrine. It was, however, accepted by Black, and its principles taught by him in Edinburgh; and before the end of the century it had practically supplanted phlogistonism in this country. Some of those who, like Kirwan, had energetically opposed the new theory ended by enthusiastically embracing it. Its introduction into Germany was mainly due to the influence of Klaproth.

We further owe to Lavoisier the recognition of the principle which lies at the basis of chemical science—the principle of the conservation of matter. Lavoisier was not the first to introduce the use of the balance into chemistry: quantitative chemistry did not actually originate with him. Boyle, Black, and Cavendish, as a matter of fact, preceded him in recognising the importance of studying the quantitative relations of substances. Nevertheless, no one before him so clearly foreshadowed the doctrine of the indestructibility of matter, and it was mainly through his teaching that the balance came to be recognised as indispensable to the pursuit of chemistry. Before his untimely death he had succeeded in impressing upon the science the main features which at present characterise it.

Lavoisier was one of the most distinguished men of his age, and his merits as a philosopher were recognised throughout Europe. Indeed, it is not too much to say that at the time of his death he was the dominant figure in the chemical world of the eighteenth century. In addition to his position as a member of the *Ferme-général*, he was made by Turgot a commissioner of the *Régie des Poudres*; and in this capacity he effected



improvements in the manufacture and refining of saltpetre, and greatly increased the ballistic properties of gunpowder. He became Secretary of the Committee of Agriculture, and drew up reports on the cultivation of flax, of the potato, and on the liming of wheat; he prepared a scheme for the establishment of experimental farms, and for the collection and distribution of agricultural implements. He introduced the cultivation of the beetroot in the Blesois, and improved the breed of sheep by the importation of rams and ewes from Spain. He was successively member of the Assembly of the Orléanais, *Député suppléant* of the States-General, and of the Commune of Paris. In 1791 he was named Secretary and Treasurer of the famous Commission of Weights and Measures, out of which grew the international system, based theoretically on a natural unit, known as the metric system, and now adopted by most civilised countries in the world. He was not only the administrative officer of the Commission: he contributed to the nomenclature of the system, and directed the determination of the physical constants on which the measurements rested, and especially the determination of the weight of the unit volume of water on which the value of the standard of mass was based. Lastly, he was Treasurer of the French Academy until its suppression in 1793 by the Convention, which shortly afterwards ordered the arrest of Lavoisier and others of the *Fermiers-généraux*—twenty-eight in all. They were sentenced to be executed within twenty-four hours, and their property confiscated. Coffinhal, who pronounced their doom, declared: "*La république n'a pas besoin de savants.*" Thus, in the fifty-first year of his age, perished the creator of modern chemistry—a victim to the senseless, sanguinary fury of the "Friends of the



LAVOISIER AND BERTHOLLET  
in the Laboratory of the Sorbonne, Paris

People." His rectitude, his public services, the purity of his private life, the splendour of his scientific achievements—all were unheeded. As Lagrange said to Delambre: "It required but a moment to strike off this head; a hundred years may not suffice to reproduce such another."

Of the men who were associated with Lavoisier in the creation of what was known at the period as the antiphlogistic chemistry, the most eminent was Berthollet.

**Claude-Louis Berthollet** was born in Savoy in 1748, and, after a medical education, became physician to the Duke of Orleans. Devoting himself to chemistry, in 1781 he was made a member of the Academy, and he became Government Commissary and Director of the Gobelins, the chief tinctorial establishment of France. Although in the main in agreement with Lavoisier, he never wholly subscribed to the idea that all acids contained oxygen. He discovered the bleaching power of chlorine, prepared potassium chlorate, and investigated prussic acid and fulminating silver.

In his *Statique Chimique*, published in 1803, he combated the partial and imperfect views of Bergman and Geoffroy with regard to the operation of chemical affinity, and showed that the direction of a chemical change is modified by the relative proportion of the reacting substances and the physical conditions—temperature, pressure, etc.—under which the change is effected. He was one of the first to draw attention to a class of phenomena known as reversible reactions, and gave a number of instances of their occurrence. Berthollet pushed his conclusions so far that he was led to doubt that chemical combination took place in fixed and definite proportions; and his views

gave rise to a memorable controversy between him and Proust, in which the latter eventually triumphed.

Berthollet enjoyed a great reputation in his time, and played a considerable part in the political history of his country. It was largely to his zeal, sagacity, and skill in developing her internal resources at a critical period when she was hemmed round by foreign troops and her ports blockaded by British ships, that France was saved from conquest. His life was more than once in jeopardy when France was governed by a Committee of Public Safety; but his honesty, sincerity, and courage even impressed Robespierre, and he escaped the perils of the Great Terror. He was an intimate friend of Napoleon, and accompanied him to Egypt as a member of the Institute. He died at Arcueil in 1822.

Davy, who visited him at his country house in 1813, says of him :—

Berthollet was a most amiable man; when the friend of Napoleon, even, always good, conciliatory, and modest, frank and candid. He had no airs, and many graces. In every way below La Place in intellectual powers, he appeared superior to him in moral qualities. Berthollet had no appearance of a man of genius; but one could not look on La Place's physiognomy without being convinced that he was a very extraordinary man.

Other notable men of this period were Fourcroy, Vauquelin, Klaproth, and Proust.

**Antoine-Francois Fourcroy**, the son of a pharmacist, was born at Paris in 1755, and started his career as a dramatic author. On the advice of Vicq-d'Azir, the anatomist, he turned to medicine, and in 1784, by the influence of Buffon, obtained the chair of Chemistry at the Jardin du Roi, in succession to Macquer. He was an excellent teacher—clear, orderly,

and methodical. He had, indeed, a talent for oratory. This he assiduously cultivated, and became one of the most popular lecturers of his time in France. Ambitious and time-serving, he became embroiled in the turbulent politics of the period, and, after a chequered career, died, embittered and disappointed, in the fifty-fourth year of his age. His chief services to science consisted in his works, *Système des Connaissances Chimiques* and *Philosophie Chimique*. These, no less than his public lectures, did much to popularise the doctrines of Lavoisier among his countrymen.

**Louis Nicolas Vauquelin**, the son of a Norman peasant, was born in 1763, and while a boy became assistant to an apothecary in Rouen. In 1780 he came to Paris, and entered Fourcroy's laboratory. Much of the experimental work published in Fourcroy's name was actually done by Vauquelin. He became a member of the Academy in 1791, Professor of Chemistry at the Mining School, Assayer to the Mint, and subsequently Professor of Chemistry at the Jardin des Plantes. On Fourcroy's death he was made Professor of Chemistry of the Medical Faculty of Paris. Vauquelin was no theorist; he was, however, an excellent practical chemist, and one of the best analysts of the period. He made a large number of mineral analyses, more particularly for Haüy, the crystallographer. He discovered the element *chromium* in the so-called red-lead ore (lead chromate) from Siberia. He also first made known the existence of *glucinum* in beryl. He described a method of separating the platinum metals, and worked upon *iridium* and *osmium*. He investigated the *hyposulphites*, *cyanates*, and *malates*. He discovered the presence of *benzoic acid* in the urine of animals; with Robiquet, he first isolated *asparagin*; with Buniva,

*allantoic acid*; and with Bouillon de la Grange, *camphoric acid*.

Vauquelin lived wholly for science, and had no other interests than in his laboratory. He was pensioned in 1822, and died at his birthplace—St. André d'Héberlot—in the sixty-sixth year of his age.

**Martin Heinrich Klaproth**, born in 1743 at Wernigerode, in the Hartz, began life, like Vauquelin, as an apothecary's apprentice at Quedlinburg. Thence he went to Hanover, and ultimately to Berlin, where he studied under Pott and Marggraf and entered the pharmacy of Valentine Rose, father of Heinrich Rose, the distinguished chemist, and Gustav Rose, the mineralogist. In 1788 he became a member of the Berlin Academy, and, on the creation of the Berlin University in 1809, was made Professor of Chemistry. As already stated, he was the first chemist of eminence in Germany to adopt the antiphlogistic theory. He was distinguished as an analyst. He discovered *tellurium*, analysed *pitchblende* and *uranil*, and first made known the existence of *uranium*, *zirconium*, and *cerium*, which he termed "ochroita." He analysed *corundum*, and was an independent discoverer of *titanium* and *glucinum*, termed by him *beryllium*. He made a large number of analyses of minerals, such as leucite, chrysoberyl, hyacinth, granite, olivin, wolfram, malachite, pyromorphite, etc. He continued actively at work until his death, in the seventy-fourth year of his age.

Analytical chemistry is under great obligations to Klaproth. He established a standard of accuracy never before approached; and much of his analytical work, both as regards processes and results, is of permanent value.

**Joseph Louis Proust**, the son of a pharmacist, was

born at Angers in 1761. He received his early training in chemistry from his father, and, after studying under Rouelle in Paris, obtained an appointment at the Salpetrière. Proust has the credit of being the first chemist to make a balloon ascent—in a Montgolfier balloon with Pilâtre de Rozier. On the invitation of the King of Spain, he went to that country to superintend certain chemical manufacturing processes. He became Professor of Chemistry at the University of Salamanca, and subsequently went to Madrid, where he was installed in a well-equipped laboratory to enable him to examine the mineral riches of Spain. On the breaking out of war his work was interrupted, and he was obliged to leave Madrid. His laboratory was completely destroyed, and his valuable collection of apparatus and specimens dissipated. Through the good offices of Berthollet, Proust was offered a considerable sum of money by Napoleon in order to induce him to turn his discovery of grape sugar to practical account. Proust was, however, too broken in health to undertake the work of a factory manager, and he retired to Mayence. On the restoration of the Monarchy he was made a member of the French Academy, his honorarium as an Academician being augmented by a pension from Louis XVIII. He died in 1826, while on a visit to Angers, his native place.

Proust is the discoverer of what is now styled "the law of constant proportion," which states that the same body is invariably composed of the same elements, united in the same proportion. He was a skilful analyst, and made numerous analyses of minerals; and he was one of the earliest to undertake a systematic study of metallic salts of organic acids.

## CHAPTER IX.

### THE ATOMIC THEORY

THE opening years of the nineteenth century were made memorable by the promulgation of the atomic theory by John Dalton. The enunciation of this theory, which affords a simple and adequate explanation of the fundamental laws of chemical combination, marks an epoch in the history of chemistry.

It may be desirable to trace, as briefly as possible, the successive steps which led up to the generalisation which more than any other has served to stamp chemistry as an exact science. That matter was *discrete*—that is, that it was not continuous, but was composed of ultimate particles—was, as already stated, imagined by the ancients, and was part of the philosophy of Leukippus, Demokritus, and Leucetius. But this supposition, although favoured by Newton and other thinkers, had little or no scientific basis prior to the middle of the eighteenth century. From that time onward a variety of chemical facts gradually accumulated, many of which at the time of their discovery had no obvious connection with pre-existing facts. It was reserved for Dalton to point out how an extension and more precise definition of the old doctrine would suffice to connect and explain them.

The first germ of an atomic theory based on chemical fact may be traced in the observation of **Tobern Bergmann** (b. 1735, d. 1784), Professor of Chemistry at Upsala, that neutral solutions of certain metals in



contact with other metals gave a precipitate without the neutrality of the solution being disturbed, and without gas being evolved. One metal had simply replaced the other in solution. Bergman thus incidentally discovered the fact of the chemical equivalence of metals. He was of opinion, however, that the phenomenon meant a transference of phlogiston from one metal to another, and that the process might be made a mode of determining the relative amount of phlogiston in various metals. Lavoisier extended Bergman's observations, and sought to show, in effect, that the process afforded a means of determining the amounts of the several metals which combined with one and the same quantity of oxygen. But neither Bergman nor Lavoisier really grasped the idea of equivalence as we understand it to-day. It began to be appreciated as the result of the work of **Jeremiah Benjamin Richter** (b. 1762, d. 1807) and of **G. E. Fischer** on the mutual action of salts in solutions, and on the determinations of the amounts of acids and bases which respectively combine with one another. Methods of measurement of the proportions in which substances combine were grouped by Richter under the term *Stöchiometry*.

However desirable it may be in the interests of history to indicate the sequence of the surmises and facts which preceded the formulation of the atomic theory, it is very doubtful whether Dalton was, to any material extent, influenced by them. A self-educated man of lowly origin, sturdily independent and highly original, he was accustomed to rely upon his own faculty of observation and experiment for his facts, and upon his own intellectual powers and mental energy for their interpretation.

**John Dalton**, the son of a Quaker hand-loom weaver,

was born at Eaglesfield, in Cumberland, in 1766. While still a boy he took to school-teaching, and acquired, in his leisure and by his own exertions, a competent knowledge of mathematics and physical science. In 1793 he was called to give instruction in mathematics, natural philosophy, and chemistry at the Manchester New College, the Nonconformist academy—now moved from Warrington—in which Priestley had formerly lectured. Here he remained six years, leaving the college to take up an independent position as a private tutor, so as to enable him the more freely to pursue his scientific inquiries. In 1800 he became Secretary of the Philosophical Society of Manchester, and remained connected, as an official, with that institution until his death in 1844. The greater number of his scientific communications were published by that society. In the outset of his scientific career he was attracted to meteorology; and it was probably its problems which led him in the first place to experiment, and to speculate on the physical constitution of gases. In the course of these observations he was led to the discovery of the law of thermal expansion of gases, with which his name is now generally associated. His speculations concerning the physical constitution of gaseous substances, arising from the contemplation of gaseous phenomena, led him to the conception that a gas is composed of particles that repel one another with a force decreasing as the distance of their centres from each other; and it is probable that in this manner he familiarised himself with the idea of the existence of atoms. His first insight into the laws of the chemical combination of these atoms seems to have originated from his discovery that, when two substances unite in different proportions, these proportions may be expressed in simple



**JOHN DALTON.**

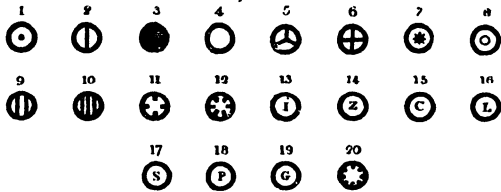
**From a painting by B. R. Faulkner in the possession of the Royal Society**

multiples of whole numbers. Thus he found, on examining the composition of marsh gas and of ethylene, both hydrocarbons, that for the same weight of hydrogen there was twice the amount of carbon in ethylene that there was in marsh gas. He then examined the oxides of nitrogen, and found a similar regularity to hold good in these compounds. Some time prior to the autumn of 1803 Dalton was led to the supposition that these regularities could be satisfactorily explained by the assumption that matter is composed of atoms having sizes and weights differing with each substance, but of identical weight and size for any particular substance, and that chemical combination consists in the approximation of these atoms. This simple hypothesis explained all the facts then known. It explained the constancy in the chemical composition of substances, which may be said to have been established by Proust, and which is now formulated as the Law of Constant Proportion—that the same body is invariably composed of the same elements, united in the same proportion. It explained also the fact discovered by Dalton that, when an element unites with another in different proportions, the higher proportions are multiples of the lowest—now formulated as the Law of Multiple Proportion. It further explained the fact, which may be said to have been foreshadowed by Richter, that when two bodies, A and B, separately combine with a third body, C, the proportions of A and B which unite with C are measures or multiples of the proportions in which A and B combine together. This is known as the Law of Reciprocal Proportion.

Dalton's theory was first made generally known by Thomas Thomson, in the third edition of his *System of Chemistry*, published in 1807, and was employed by

# ELEMENTS

## *Simple*



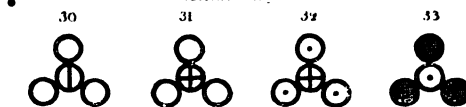
## *Binary*



## *Ternary*



## *Quaternary*



## *Quinquenary & Sextenary*



## *Septenary*



The illustration on the preceding page contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Fig.		Fig.	
1.	Hydro. its rel. weight . . . . .	11.	Strontites . . . . .
2.	Azote . . . . .	12.	Barytes . . . . .
3.	Carbone or charcoal . . . . .	13.	Iron . . . . .
4.	Oxygen . . . . .	14.	Zinc . . . . .
5.	Phosphorus . . . . .	15.	Copper . . . . .
6.	Sulphur . . . . .	16.	Lead . . . . .
7.	Magnesia . . . . .	17.	Silver . . . . .
8.	Lime . . . . .	18.	Platina . . . . .
9.	Soda . . . . .	19.	Gold . . . . .
10.	Potash . . . . .	20.	Mercury. . . . .
21.	An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight . . . . .		8
22.	An atom of ammonia, composed of 1 of azote and 1 of hydrogen . . . . .		6
23.	An atom of nitrous gas, composed of 1 of azote and 1 of oxygen . . . . .		12
24.	An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen . . . . .		6
25.	An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen . . . . .		12
26.	An atom of nitrous oxide, 2 azote + 1 oxygen . . . . .		17
27.	An atom of nitric acid, 1 azote + 2 oxygen . . . . .		19
28.	An atom of carbonic acid, 1 carbone + 2 oxygen . . . . .		19
29.	An atom of carburetted hydrogen, 1 carbone + 2 hydrogen . . . . .		7
30.	An atom of oxynitric acid, 1 azote + 3 oxygen . . . . .		26
31.	An atom of sulphuric acid, 1 sulphur + 3 oxygen . . . . .		34
32.	An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen . . . . .		16
33.	An atom of alcohol, 3 carbone + 1 hydrogen . . . . .		16
34.	An atom of nitrous acid, 1 nitric acid + 1 nitrous gas . . . . .		31
35.	An atom of acetous acid, 2 carbone + 2 water . . . . .		26
36.	An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water . . . . .		33
37.	An atom of sugar, 1 alcohol + 1 carbonic acid . . . . .		35

Thomson in his paper on "The Oxalates of Strontium," published the same year in the *Philosophical Transactions*. The first printed account by Dalton himself is contained in Part I. of his *New System of Chemical Philosophy*, published in 1808, the substance of which had been previously given in a course of lectures at the Royal Institution, London, and subsequently repeated in Edinburgh and Glasgow.

The statement of his theory is contained in chapter iii. of this work, under the heading "Of Chemical Synthesis," and is accompanied by a plate and explanation, of which a facsimile is given on pp. 100-1.

The facts upon which Dalton based his theory are incontrovertible; but Dalton's explanation of them was not universally accepted at the time he gave it. Davy, who, of course, was familiar with the conception of atoms as part of the Newtonian philosophy, objected to the term "atomic weight" introduced by Dalton, and suggested the expression "combining proportion"; and Wollaston, for similar reasons, proposed the term "equivalent," as denoting the constant quantity with which bodies went in and out of combination. There is no doubt that the use of these terms retarded the general acceptance of Dalton's doctrine, and, moreover, brought into the science a confusion which was not finally dispelled, as we shall see, until during the second half of the century.

Dalton's estimations of the relative weights of the atoms, or, to use Davy's phrase, the values of their combining proportions, were, as might be expected, very rough approximations to the truth. This arose partly from inadequate experimental data, and partly from uncertainty as to the relative number of the constituent atoms which made up a compound. Neither

Dalton nor his immediate successors had any rational or consistent method of determining the latter point. The view taken of the composition of the compound decided what particular multiples or sub-multiples of the values of the atomic weights of its constituents were to be adopted. As Dalton, in many cases, had no real criterion to guide him, he made the simplest possible assumptions; but these might or might not be valid; and subsequent experience showed that in some cases they were erroneous.

It was, however, generally recognised that these atomic weights, combining proportions, or equivalents, as they were for a time indifferently termed, were chemical constants of the highest importance, both to the scientific chemist, who, apart from their theoretic interest, had need of them in the course of quantitative analysis, and to the manufacturing chemist, who required them for the intelligent exercise of his operations; and accordingly a number of chemists, very shortly after the promulgation of Dalton's theory, attempted to determine their values with all possible precision. Chief among these was the Swedish chemist Berzelius, to whom science was indebted for a series of estimations of atomic weights, which were long regarded as models of quantitative accuracy, and stamped their author as the greatest master of determinative chemistry of his age.

**Jöns Jakob Berzelius**, the son of a schoolmaster, was born near Linköping, in East Gothland, Sweden, in 1779. Entering Upsala with a view to the profession of medicine, he was attracted, under the influence of Afzelius—or, rather, in spite of it—to the study of chemistry, and, later, of voltaic electricity, then in its infancy. While holding a number of minor appointments



as a teacher of medicine, pharmacy, physics, and chemistry, he was elected, in 1808, a member of the Swedish Academy of Sciences, of which he became President in 1810. In 1818 he was made permanent Secretary of the Academy, and, by means of a yearly subsidy, was enabled to devote himself wholly to experimental science. He was ennobled in 1818, and on the occasion of his marriage, in 1835, was created a baron of the Scandinavian kingdom. He died in 1848.

Berzelius occupies a pre-eminent position in the history of chemistry, and during a considerable portion of his lifetime exercised an almost unassailable authority as a chemical philosopher. He is distinguished as an experimenter, as a discoverer, as a critic and interpreter, and as a lawgiver. His contributions to chemical knowledge range over every department of the science. He shares with Davy the honour of having established the fundamental laws of electro-chemistry. His experimental work on the atomic weights of the elements—the great work of his life—was of supreme importance at this particular period of the development of chemistry: it served not only to give precision to, and enhance the significance and value of, Dalton's generalisation, but it furnished chemists, for the first time, with a set of constants, ascertained with the highest exactitude of which operative chemistry was then capable, thereby contributing to the expansion of quantitative analysis, and to a more exact knowledge of the composition of substances. Berzelius, indeed, was an analyst of the first rank—conscientious, patient, and painstaking; an ingenious and skilful manipulator; inventive and resourceful. What determinative chemistry owes to his labours, and not less to his example, is obvious from even the most superficial



JÖNS JAKOB BERZELIUS.  
From a painting by J. G. Sandberg.

examination of its literature during the first third of the last century.

As a discoverer, Berzelius first made known the existence of *cerium* (1803), of *selenium* (1818), and of *thorium* (1828); and he prepared and investigated a large number of their combinations. He isolated *silicon* (1823), *zirconium* (1824), *tantalum* (1824), and studied the compounds of *vanadium*, discovered by his countryman Sefström. He largely extended our knowledge of groups of substances in which sulphur replaces oxygen; investigated compounds of fluorine (1824), platinum (1828), and tellurium (1831-33), and made many analyses of minerals, meteorites, and mineral-waters. He discovered *racemic acid* and investigated the ferrocyanides. It was his investigation of racemic acid—which has the same percentage composition as tartaric acid—that first enabled him to grasp the conception of *isomerism*, a term which we owe to him, and of *metamerism* and *polymerism*. He was the first to study the phenomena of contact-actions, which he comprehended under the term *catalysis*.

As an author his literary activity was astonishing. His new system of mineralogy marks an epoch in the history of that branch of science. His text-book on chemistry was long the leading manual, and went through many editions, being constantly revised by him. His annual reports on the progress of physics and chemistry extended to twenty-seven volumes, and constitute a monument to his industry, thoroughness, perspicacity, and critical ability.

Although holding no university appointment, and with a laboratory of the most modest dimensions and character, Berzelius exercised great influence as a teacher. Some of the most notable chemists of the

last century, such as Heinrich and Gustav Rose, Dulong, Mitscherlich, Wöhler, Chr. Gmelin, and Mosander, were among his pupils; and many of them have testified to his stimulating power as an investigator of nature, and to his merits as a worthy, genial man.

The reasonableness of Dalton's conjecture received further support from the discovery by Gay Lussac in 1808, that gases always combine in simple proportions by volume, and that the volume of the gaseous product formed, when measured under comparable conditions of temperature and pressure, stands in a simple relation to the volumes of the constituents. The law of pressure discovered by Boyle, that of thermal expansion by Dalton, and of volumes by Gay Lussac (which, it ought to be stated, was previously and independently made by Dalton), are explained on the assumption that equal numbers of the particles—either as simple particles or as compound particles—are present in the same volume of the gas. This method of explanation was first clearly stated by the Italian physicist **Avogadro** in 1811, but its significance, as will be seen subsequently, was not appreciated until half a century later.

As the values for the atomic weights gradually became more exact, speculations arose as to the significance of the numerical relations which were observed to exist among them. In 1815 **William Prout** threw out the supposition that the atomic weights of the gaseous elements are multiples by whole numbers of that of hydrogen. Extended into a generalisation, this might be held to indicate that all kinds of matter are so many forms of a primordial substance. Subsequent inquiry showed that Prout's "Law," as it is sometimes called, was not tenable in its original form. Certain elements,

it was conclusively proved, had atomic weights which were not whole numbers. Dumas subsequently modified the law, after a redetermination of a large number of atomic weights, by assuming that the substance common to the so-called elements had a lower atomic weight than unity. Although there are a considerable number of elements whose atomic weights, based upon the most accurate determinations, are remarkably close to whole numbers, the investigations of Stas and others afford no valid reason for believing that Prout's hypothesis, and the underlying supposition to which it has been held to point, are justified by experimental evidence.

## CHAPTER X.

### THE BEGINNINGS OF ELECTRO-CHEMISTRY

THE first year of the nineteenth century is further memorable on account of the invention of the voltaic pile, and by reason of its application by **William Nicholson** and **Sir Anthony Carlisle** to the electrolytic decomposition of water. This mode of resolving water into its constituents made a great sensation at the time, mainly because of the extraordinary method by which it was effected. It afforded an independent and unlooked-for proof of the compound nature of water by a method altogether differing in principle from that by which its composition had been previously ascertained.\* The formation of water by the combustion of hydrogen brought no conviction of its real nature to a confirmed phlogistian like Priestley; and it is even doubtful whether Cavendish ever fully realised the true significance of his great discovery. But the fact that the quantitative results of the analysis thus effected were identical with those of its synthesis, as made by Cavendish and Lavoisier, admitted of only one interpretation. This cardinal discovery may be said to have completed the downfall of phlogiston.

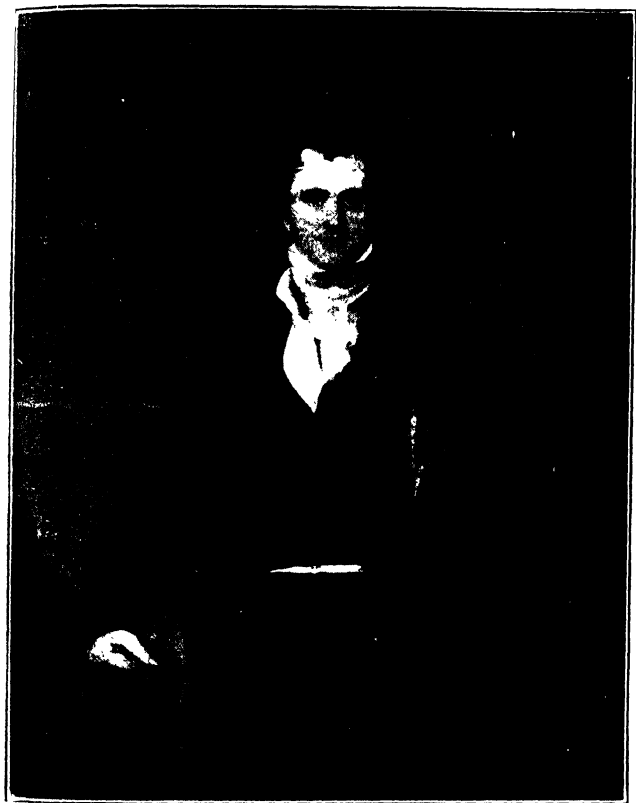
The value of the voltaic pile as an analytical agent was nowhere more quickly appreciated than in England. In the hands of Humphry Davy its application to the analysis of the alkalis and alkaline earths led to discoveries of the greatest magnitude.

**Humphry Davy** was born in Penzance in 1778. In

the course of his studies for the profession of medicine he was attracted to chemistry; and he became chemical assistant to Dr. Beddoes, a former teacher of chemistry at Oxford, but then living at Clifton, near Bristol. While in the capacity of assistant and operator in Beddoes's Pneumatical Institute, Davy discovered the intoxicating properties of *nitrous oxide* (so called laughing gas), which brought him into prominence and led to his engagement by the managers of the newly-created Royal Institution in London as lecturer in chemistry in succession to Garnett. He early began to experiment on galvanism, and soon succeeded in developing the fundamental laws of electro-chemistry; and in 1807 he effected the *decomposition of potash and soda* by the application of voltaic electricity—thereby establishing, what indeed had been surmised previously, that the alkalis are compound substances. He subsequently proved that this was also the case with the alkaline earths. Davy thus added some five or six metallic elements to those already known.

These discoveries, perhaps the most brilliant of their time, afforded additional evidence of the invalidity of Lavoisier's assumption that oxygen, as the name implies, was the "principle of acidity." The surmise, in fact, was already disproved by the case of water—a neutral substance and devoid of all the recognised attributes of an acid. It was still further disproved by the cases of potash and soda—strongly alkaline compounds.

Additional evidence was adduced by Davy in demonstrating, in 1810, that the so-called *oxymuriatic acid*, the *dephlogisticated marine acid* discovered by Scheele, contained no oxygen, but was a simple, indivisible substance. For the old designation, which connoted a compound body, he substituted the name *chlorine*, in allusion



SIR HUMPHRY DAVY.

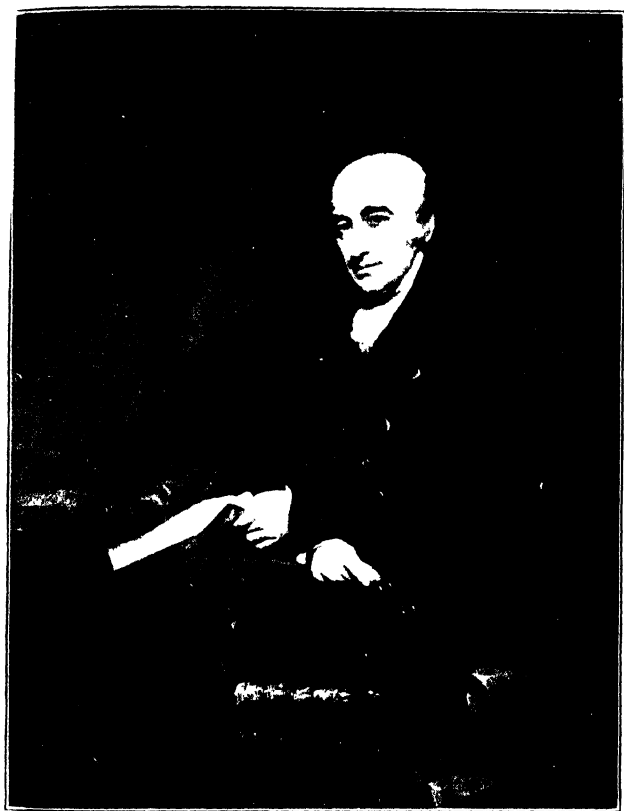
From a painting by Lawrence in the possession of the Royal Society.



to the characteristic colour of the element. In the course of his investigation on this substance he discovered the *penta- and trichloride of phosphorus*, *chlorophosphamide*, and *chlorine peroxide*. He was also the discoverer of *telluretted hydrogen* and an independent discoverer of *nitrosulphonic acid*.

He worked on *iodine* and the *iodates*, on the *diamond*, on the so-called *fuming liquor of Cadet*, on *nitrogen chloride*, and on the *pigments of the ancients*. Lastly, he invented the *miner's safety lamp*, with which his name will always be associated, effecting thereby what was practically a revolution in coal-mining. He became President of the Royal Society in 1820, and died at Geneva on May 29th, 1829, in the fifty-first year of his age. Davy was a singularly gifted man, of great mental vigour and imaginative power; quick, lively, and ingenious; an eloquent teacher and a daring and brilliant experimenter.

Another noteworthy name in the chemical history of this period is Wollaston. **William Hyde Wollaston**, born at East Dereham, in Norfolk, in 1766, was educated at Cambridge with a view to the profession of medicine, but, failing to secure a practice, he devoted himself to the pursuit of science, and especially to optics and chemistry. He devised a method of *working platinum*, and was the first to make known the existence of *palladium* and *rhodium*. He was one of the most ingenious and acute analysts of his time, and possessed remarkable inventive powers. He investigated the nature of *urinary calculi* and *chalk stones*. His paper on the *oxalates of potash* was of great service at the time as a demonstration of the law of multiple proportions. He first drew attention to the existence in the solar spectrum of what were subsequently termed



WILLIAM HYDE WOLLASTON.

From a painting by J. Jackson, R.A., in the possession of the Royal Society.

the *Fraunhofer lines*; and he invented the *reflecting goniometer* and the *camera lucida*, and a *slide rule* for chemical calculations. He resembled Cavendish in temperament and mental habitudes, and, like him, was distinguished for the range and exactitude of his scientific knowledge, his habitual caution, and his cold and reserved disposition. He died in 1828.

Almost immediately after the publication of Volta's discovery attempts were made—notably by Berzelius in Sweden and by Davy in England—to prove that electrical and chemical phenomena are correlated and mutually dependent. This assumption was more fully worked out by Berzelius in 1812, and it served as the basis of a chemical system which exercised considerable influence on chemical doctrine during the first half of the nineteenth century.

Berzelius assumed that electric polarity was an attribute of all atoms—that these were bipolar, in fact, but that in them either positive or negative electricity predominated. Hence the elements were capable of being divided into two classes—that is, positive or negative, depending upon the excess of either charge. Which of the electricities predominated might be ascertained by determining the particular pole at which the element was separated on electrolysis. Combinations of dissimilar elements—or, in other words, chemical compounds—were also endowed with polarity. The chemical affinities of elements and compounds were related to the excess of either kind of electricity resident in them; and chemical combination resulted from, and was a consequence of, the more or less perfect neutralisation of the two kinds. From a study of the electrical deportment of the elements Berzelius sought to arrange them in series, starting with oxygen as the most electro-

negative member. These conceptions were employed by him as the basis of a method of classification. The attempt is historically interesting as being the first systematic endeavour to gain an insight into the constitution of chemical compounds—that is, to determine the manner in which the constituent atoms are grouped or arranged with respect to one another, or, in other words, to distinguish between the empirical and the rational composition of substances, which is the ultimate aim of modern chemistry.

A necessary consequence of these views was that every compound was to be considered as made up of two parts in electrically different states. Thus baryta consisted of a combination of the electro-positive barium, combined with the electro-negative oxygen; it combined with sulphuric oxide because the preponderating positive electricity it contained met with the negative electricity which prevailed in the sulphuric oxide. Generalising, it may be said that the basic oxides are invariably the positive constituents of salts, whereas the acid oxides are the negative constituents, as proved by the mode in which the two kinds of oxides separated at the poles on electrolysis. Barium sulphate, then, was to be regarded as made up of two entities— $\text{BaO}$  and  $\text{SO}_3$ —and hence was to be called sulphate of baryta. Berzelius extended this conception in order to explain the formation of double salts—such, for example, as potash alum, which he regarded as a binary compound of positive potassium sulphate and negative aluminium sulphate, each of which, in its turn, could be resolved into an acidic and a basic oxide of opposite electricities.

The dualistic notions of Berzelius led him to the construction of a system of chemical nomenclature and notation which, in its main features, has persisted to

this day, and is universally current, with certain modifications, in modern chemical literature. We owe to him the grouping of the elements into metals and metalloids, and also our present system of symbolic notation, whereby even complicated chemical reactions may be expressed in a concise and intelligible manner. Chemical symbols were used by the alchemists; but Berzelius first suggested that a chemical symbol should not only represent the element to which it refers, but also its relative atomic weight. Chemical equations became quantitative as well as qualitative expressions of the facts they denote. Such equations implicitly assumed that, to use Davy's words, chemistry had passed under the dominion of the mathematical sciences. Professed mathematicians were, however, slow to recognise that the phenomena of chemical action were capable of formal mathematical treatment. Davy relates that on speaking to Laplace of the atomic theory in chemistry, and expressing his belief that the science would ultimately be referred to mathematical laws similar to those he had so profoundly and successfully established with respect to the mechanical properties of matter, the idea was treated in a tone bordering on contempt.

Berzelius's electro-chemical system, and the dualistic ideas associated with it, were of considerable service when applied to the inorganic branch of the science; but attempts to fit them to the facts of organic chemistry, which began to accumulate rapidly after the first quarter of the century, failed. Its inadequacy as a comprehensive generalisation became more and more manifest, and it eventually fell. In fact, it may be said to have received its death-blow by Davy's discovery of the elementary nature of chlorine, and by the recognition of the fact that the acids do not necessarily

contain oxygen. Davy and, later, Dulong made it obvious that, if any one element was to be regarded as the acidifying principle, it was hydrogen, and not oxygen; and, in a sense, this view ultimately prevailed in the recognition of the acids as salts of hydrogen.

In France the study of electro-chemistry was undertaken by Gay Lussac and Thénard, largely owing to the action of the Emperor Napoleon, who furnished the funds for the construction of a powerful galvanic battery. The results were published, in 1811, under the title, *Recherches Physico-Chimiques, faites sur la Pile*, etc. Gay Lussac, whose name has already been mentioned as one of the discoverers of the Law of Combination of Gases, played a considerable part in the history of chemistry at this period. He was one of the earliest to appreciate the importance of Dalton's generalisation, and to point out the significance of his own discovery in strengthening it. He was probably led, in the first instance, to the recognition of the law of gaseous combination by Berthollet's work on the volumetric composition of ammonia gas, and by his own discovery—made in 1805, in conjunction with Humboldt, in the course of their analysis of atmospheric air—that one volume of oxygen combined with exactly two volumes of hydrogen to form water. The regularities thus indicated he found to be general: all gases which are capable of chemical union combine in simple proportions by volume, and the volume of the product, if a gas, always stands in some simple relation to the volumes of the constituents.

**Joseph Louis Gay Lussac** was born in 1778, at Saint Leonard, studied chemistry in Paris, and was associated in chemical inquiry with Berthollet. As *Eleve-Ingenieur* in the *École Nationale des Ponts et des*

Chaussées he began the experimental work in physics and chemistry upon which his fame rests. In 1804 he undertook, with Biot, a series of balloon ascents for the purpose of investigating the physics and chemistry of the upper regions of the atmosphere. In 1806 he became Professor of Chemistry at the École Polytechnique, and in 1832 Professor at the Jardin des Plantes. He was one of the chief assayers of the French Mint, and, as member of many commissions, exerted considerable influence in official circles. He died in 1850.

Gay Lussac and Thénard were the first to devise a method of obtaining potassium and sodium by a purely chemical process, whereby these metals could be procured in far larger quantities than was at that time possible by electrolytic means. They were thus enabled to make use of the strong deoxidising power of these metals to effect a number of reductions, notably that of boric oxide to *boron*. Gay Lussac and Thénard were also the first to make known the existence of *boron fluoride*. We further owe to Gay Lussac the discovery of *cyanogen*, the first of the so-called compound radicals. He first prepared ethyl iodide, investigated sulphovinic acid and grape sugar, studied etherification and fermentation, etc. We are also indebted to him for a method of determining vapour densities which proved of great service in ascertaining the molecular weights of substances. He worked on iodine and its compounds, discovered, with Welter, *thiosulphuric acid*, and investigated fulminic acid in collaboration with Liebig.

Among his services to analytical chemistry were his method for the analysis of gunpowder, his volumetric estimation of silver (wet silver assay), chlorometric analysis, alkalimetry, etc. He devised the system still

in use in France for the estimation of alcohol in spirits of wine.

**Louis Jacques Thénard** was born in 1777 at Nogent-Sur-Seine, and was a pupil of Vauquelin and of Berthollet. In 1797 he became *répétiteur* at the Polytechnic School of Paris, and eventually its professor. He subsequently occupied the chair of chemistry at the Collège de France, and of the Faculty of Science of the University of Paris. He was ennobled by Charles X. in 1824, and died at Paris in the eightieth year of his age.

In addition to his work with Gay Lussac already mentioned, we owe to Thénard the discovery of *hydrogen peroxide* and *hydrogen persulphide*. Together with Dulong he studied the catalytic action of platinum on mixtures of oxygen and hydrogen. He investigated the fatty acids, and worked on fermentation and on ether-formation; and he was the first to isolate citric and malic acids. He also occupied himself with the chemistry of bile, perspiration, albumen, the acids of urine and milk, and with the theory of mordants.

In 1834 Faraday made known the important fact that on passing the same galvanic current through a number of electrolytes—water, hydrochloric acid, solutions of metallic chloride—these were decomposed in such manner that definite amounts of hydrogen or metal were separated at the negative pole, and corresponding amounts of oxygen or chlorine were evolved at the positive pole. These observations were comprehended by Faraday under his “law of definite electrolytic action.” The electro-chemical equivalents thus obtained were in some cases identical with the atomic weights deduced by Berzelius; in others they were not; but, nevertheless, when they differed, they stood in some simple relation to the assumed atomic weight. The



significance of Faraday's observation was not lost sight of, although his anticipation that the determination of electro-chemical equivalents would be of use in fixing atomic weights was not immediately appreciated. A clear distinction between the *equivalent*, the *atom*, and the *molecule* was not then apprehended. As will be subsequently shown, it was only during the latter half of the nineteenth century that the discrepancies and inconsistencies thus revealed were definitely reconciled and cleared up.

## CHAPTER XI.

### THE FOUNDATIONS OF ORGANIC CHEMISTRY

As the horizon of chemistry widened and its operations extended, it became necessary to treat its subject-matter methodically. Accordingly attempts were made in the various systematic treatises which began to appear in the seventeenth century to group its facts into an orderly and rational arrangement. One of the earliest of such systematic treatises was the *Cours de Chimie* of Nicolas Lemery, published in 1675. Although this work was styled by Boerhaave "a tumultuary mass of pharmaceutical processes, without any certain design or coherence," it is noteworthy as being the first of its kind to divide the science into its present main branches of inorganic and organic chemistry.

It may be desirable to indicate, as briefly as possible, the general state of knowledge respecting the chemistry of organic substances down to the early years of the last century. As already mentioned, such substances as acetic acid, turpentine, starch, sugar, certain dye stuffs, and oils, had long been known; and such processes as saponification and fermentation had been practised from very early times. The alchemists had prepared a variety of essential oils, aliphatic ethers, and esters; and the iatro-chemists had obtained benzoic and succinic acids, and acetic acid from wood. Milk sugar was first prepared by Fabrizio Bartoletti in 1619. Grape

sugar was first mentioned as occurring in honey by Glauber in 1660. Boyle first detected the presence of a spirit among the products of the destructive distillation of wood. Few of the followers of Stahl occupied themselves with organic products; and it was only towards the end of the phlogistic period that attention was once more directed to products of animal and vegetable origin. Scheele isolated glycerin in 1784, and obtained *ethyl chloride* by the distillation of a mixture of common salt, pyrolusite, oil of vitriol, and alcohol. *Ethyl acetate* was first prepared by Lauraquais in 1759. Arvidson obtained *ethyl formate* in 1777. *Oxalic ether* was first made by Savary in 1773. What was long known as *oil of wine* appears to have been first mentioned by Libavius, but its true nature was discovered by Hennel in 1826. The formation of *aldehyde* was first recognised by Scheele in 1774, and it was in turn investigated by Fourcroy and Vauquelin, Döbereiner, and Gay Lussac; but it was first definitely isolated in 1835 by Liebig, who gave it its name.

The first organic acid known was vinegar (acetic acid), and for a long time all naturally occurring organic acids having a sour taste were regarded as identical with or as forms of vinegar. It was only during the second half of the eighteenth century that it was clearly ascertained that a variety of organic acids exist, perfectly distinct from acetic acid. *Glacial acetic acid* was first obtained by Löwiz in 1789. Acetic acid, as a product of the destructive distillation of wood, was first obtained by Götting in 1779. The acetic fermentation has been studied from very early times. Surmises as to the mode in which wine was converted into vinegar are to be met with in the works of Basil Valentine, Becher (1669), Lemery (1675), and Stahl (1667). Priestley, for a time,

held the opinion that vinegar contained a vegetable acid air, but he subsequently discovered and corrected his error. The direct conversion of spirit of wine (ethyl alcohol) into acetic acid was studied by Lavoisier and Berthollet, who first clearly recognised that it was a process of oxidation. The quantitative composition of acetic acid was first established by Berzelius in 1814. Many of the acetates have been known from early times. *Verdigris* is mentioned by Theophrastus, Dioscorides, and Pliny. *Zinc acetate* was known to Geber, and *potassium acetate* to Pliny, who mentions its use in medicine. *Ammonium acetate* was also used in medicine as far back as the beginning of the seventeenth century, and was particularly recommended by the physician, Raymond Minderer. *Sodium acetate* was prepared by Duhamel in 1736. *Lead acetate* was known in the fifteenth century, and was styled by Libavius *saccharum plumbi quintessentiale*, in allusion to its sweet taste. What was called by the alchemists *lac virginis* was a turbid solution of basic lead acetate, and it was frequently used in medicine, more particularly by Goulard in 1760. What we now call *acetone* was first observed by Libavius, in 1595, and subsequently by Boyle, during the destructive distillation of lead acetate: its formation from other acetates was noticed by Trommsdorff, Derosne, and Chenevix, by whom it was termed pyroacetic spirit. Its true nature and composition were first ascertained by Liebig in 1831.

The formation of tartar in the manufacture of wine has been known from the earliest times. It was regarded as, and originally styled, the *fuex vini*. The word "Tartarus" is first met with in alchemistic literature in the eleventh century, and is the Latinised form of an Arabic word. Marggraf, in 1764, recognised that

the tartar of wine contained potash ; but tartaric acid itself was first isolated by Scheel  in 1769.

The *double tartrate of potash and soda* was first prepared in 1672 by Peter Seignette, an apothecary of Rochelle, and was used by him in medicine. *Tartar emetic* was discovered by Adrian von Mynsicht in 1631, and its true nature explained by Bergmann in 1773. *Racemic acid* was first mentioned by a wine manufacturer named Kestner, and was recognised as an acid in 1819. Its relation to tartaric acid, with which it is isomeric, was first explained by Berzelius, who gave it its name.

The naturally occurring oxalates were long considered as identical with tartar. *Oxalic acid* was obtained by Scheele in 1776 by means of the action of nitric acid upon sugar. This acid was further investigated by Bergmann, who observed its decomposition by heat with the formation of a gas burning with a blue flame. The identity of the naturally occurring oxalic acid with that prepared from sugar was established by Scheele in 1784. The quantitative composition of oxalic acid was first ascertained by Dulong in 1815. *Mucic acid* was discovered by Scheele in 1780, and was studied by Fourcroy, who gave it the name it now bears. *Pyromucic acid* was also known to Scheele, and was observed by Hermhst dt and Houton-Labillardiere. *Camphoric acid* was first recognised by Bouillon-Lagrange and Vauquelin. *Suberic acid* was discovered by Brugnatelli in 1787.

That gum benzoin yielded a product (*benzoic acid*) by sublimation was known in the sixteenth century. It was introduced into medicine by Turquet de Mayerne as *flowers of benzoin*. Scheele showed how this acid might be obtained by wet methods from gum-benzoin. It was detected in Peru-balsam by Lehmann in 1709. Rouelle found it in the urine of the cow and the camel.

Liebig, in 1829, detected the difference between *hippuric acid* and benzoic acid. The characteristic acid in amber (*succinic acid*) was first detected by Pott in 1753.

*Formic acid* was first isolated by Wray in 1676. *Lactic acid* was discovered by Scheele in sour milk in 1780. For a time it was regarded as impure acetic acid, until it was detected in muscle juice by Berzelius, and its individuality established. Its true composition was ascertained by Mitscherlich and by Liebig in 1832. *Citric acid* has been known since the thirteenth century, but it was first definitely isolated by Scheele in 1784. Apple juice was used in medicine in the sixteenth century, and the soda salt of its characteristic acid (*malic acid*) was prepared by Donald Monro in 1767.

It was known to the ancients that extract of gall nuts acquired a black colour when mixed with a solution of iron vitriol; and Boyle and Bergmann ascribed this phenomenon to the presence of a peculiar acid. *Gallic acid* was first isolated by Scheele in 1785, and its composition established by Berzelius in 1814. *Tannic acid* was definitely recognised as distinct from gallic acid by Seguin in 1795.

Mellite, or honey-stone, is mentioned in mineralogical treatises in the sixteenth century. That it consisted of the alumina salt of a special acid (*mellic acid*) was shown by Klaproth in 1799.

*Prussian blue* was accidentally discovered in 1710 by a dyer named Diesbach. Its mode of manufacture was first made known by Woodward in 1724. The peculiar reaction by which it was obtained was made the subject of investigation by many chemists of the period without any decisive result. Scheele observed that, when the salt which occasioned the blue colour with vitriol was distilled with sulphuric acid, a volatile acid, inflammable

and soluble in water, was obtained. This acid received from Bergmann the name of *acidum cœrulei berolinensis*, or "Berlin-blue acid," subsequently shortened by Guyton de Morveau to *prussic acid*. Scheele also prepared the cyanides of silver and ammonium. That prussic acid was free from oxygen was established by Berthollet. Anhydrous prussic acid was first obtained by Von Ittner, who first established its highly poisonous nature. Bolin, in 1802, had previously observed the presence of prussic acid in oil of bitter almonds, the poisonous character of which was known to Dioscorides. Porret first definitely isolated *potassium ferrocyanide*, and subsequently discovered the *thiocyanates*, the quantitative composition of which was ascertained by Berzelius in 1820. That prussic acid was a compound of hydrogen and cyanogen was established by Gay Lussac in 1815.

*Cyanic acid* was discovered by Wöhler in 1822, in which year also L. Gmelin discovered the *ferricyanides*.

*Fulminating mercury* was first prepared by Howard in 1800, and *fulminating silver* by Brugnatelli in 1802. These were recognised by Liebig, in 1822, to contain a peculiar acid, which he termed *fulminic acid*, and which he showed to have the same composition as the cyanic acid discovered by Wöhler. *Uric acid*, so named by Fourcroy, was discovered in gall stones by Scheele in 1776. *Urea* was first definitely isolated by Fourcroy and Vauquelin in 1799, and was synthetically prepared by Wöhler in 1828.

The bitter principles of plants and their medicinal virtues early attracted attention; but the first attempt to isolate them was made by Fourcroy and Vauquelin in the case of the Peruvian bark, long known for its power as a febrifuge. In 1806 Vauquelin obtained *quinic acid*. *Cinchonine* was first isolated by Gomes in 1811.

The chemical nature of opium was the subject of numerous inquiries in the early years of the nineteenth century. In 1805 Sertürner detected the existence of *meconic acid*, and in 1817 that of *morphine*, which he recognised as an alkaloid. *Narcotine* was discovered by Robiquet in 1835. The investigation of other bitter substances was undertaken by Pelletier and Caventou, who in 1818 discovered *strychnine*, *brucine* (1819), and *veratrine* (1820).

The contemporaries and immediate followers of Lavoisier were the first to make a systematic attempt to elucidate the chemical nature of organic products of animal origin. To this period belongs the work of Fourcroy and Vauquelin on animal chemistry. Chevreul, a pupil of Fourcroy, worked on urine, adipocire, and the animal fats in the first decade of the last century. Kirchhoff, in 1811, discovered the method of converting starch into sugar; and Döbereiner, in 1822, described a method of preparing formic acid artificially. Dumas and Boullay, in 1827-1828, prepared a number of new derivatives of ethyl alcohol; and in 1834 Dumas and Peligot studied in like manner the chemistry of methyl alcohol, and pointed out many analogies which their compounds possessed, not only among themselves, but also to inorganic substances.

Although a considerable amount of information as to the existence, modes of occurrence, and properties of bodies found in the animal and vegetable kingdoms had been accumulated by the end of the first quarter of the nineteenth century, no serious attempt was made to study them systematically until after that period. In fact, they were not even regarded as coming within the operations of laws found to be applicable to the products of the inorganic world, by the investigation



of which products, indeed, those laws had been discovered.

Down to 1828 it was considered that inorganic and organic substances were sharply differentiated by the circumstance that, whereas the former might be prepared by artificial means, and even built up from their elements by synthetic processes in the laboratory, the latter could only be formed in the bodies of animals and plants as the result of vital force. In that year Wöhler showed that urea, pre-eminently a product of animal metabolism, could be prepared synthetically from inorganic materials. Other instances of a similar kind were discovered in rapid succession; and the idea that organic substances could alone be formed by vital processes was proved to be invalid. Moreover, large numbers of substances of a character analogous to those produced by physiological action, but not known to occur in the animal or vegetable kingdom, were prepared. There is, therefore, no absolute distinction to be drawn between the chemistry of the inorganic and organic worlds.

At the present day we mean by "organic compounds" simply the compounds of carbon. These are so numerous, and frequently so complex, that it is convenient to group them together, and study them as a special section of the science. At the outset it was supposed that only very few elements entered into the composition of organic substances. This, indeed, was held to be a point of fundamental distinction between organic and inorganic compounds. Lavoisier was of opinion that all organic bodies were combinations of carbon, hydrogen, and oxygen. Berthollet first discovered the presence of nitrogen in a product of animal origin. Sulphur and phosphorus were detected later.

There is apparently no *à priori* reason why any element should not be associated with carbon, and enter into the composition of an organic compound.

Lavoisier was one of the first to devise methods for ascertaining the composition of organic (carbon) compounds, and to indicate the general principles by which the proportion of the elements met with in these substances can be ascertained. So imperfectly, however, were these methods worked out that it was not established until the close of the first decade of the nineteenth century that organic compounds even obeyed the law of multiple proportions. Thanks to the efforts of Berzelius, Gay Lussac, and Thénard, and especially of Liebig, in 1830, methods of organic analysis were so far perfected that it became possible to ascertain the empirical composition of these compounds with certainty. This point reached, the development of this section of chemistry proceeded with unexampled rapidity. Not only was the composition of numbers of products, such as sugar, starch, the vegetable acids, certain alkaloids, etc., established, but altogether unlooked-for facts became manifest. One of the most surprising of these was that of *isomerism*.

Up to the close of the first quarter of the nineteenth century it seemed self-evident that substances of the same percentage composition are necessarily identical. In 1823 Liebig showed that the silver cyanate of Wöhler had the same composition as silver fulminate. Faraday, in 1825, found a hydrocarbon in oil gas, which had the same composition as olefiant gas, but was otherwise different from it; and in 1828 Wöhler discovered that urea and ammonium cyanate—perfectly dissimilar substances—were identical in elementary composition. Lastly, Berzelius found this to be true of tartaric and

racemic acids; and he thereupon proposed the term *isomerism* to denote the general fact. He further pointed out that the phenomenon could only be explained by supposing that the relative positions of the atoms in isomeric compounds are different.

But the influence of molecular or atomic grouping in determining the specific character of a substance is not confined to compounds. The same phenomenon is observed to occur among the elements. It was conclusively established by Lavoisier that the diamond and charcoal are chemically the same thing—both forms of carbon. Scheele showed that graphite was a third form of carbon. Phosphorus, sulphur, and oxygen were subsequently shown to be each capable of existence in various modifications. Instances of this character were grouped together in 1841 by Berzelius under the term *allotropy*.

The recognition of the fact of isomerism exerted a great influence on the development of organic chemistry. It ultimately led to the assumption that particular groups of elements or atomic complexes, so-called *radicals*, were to be found in organic compounds—a conception based originally on Gay Lussac's discovery of *cyanogen*, a combination of carbon and nitrogen, which was found to behave like a simple substance, such as chlorine, and to give rise to compounds analogous to the corresponding chlorides. This idea of the existence of compound radicals was greatly strengthened by a memorable investigation by Liebig and Wöhler, in 1832, on oil of bitter almonds and its derivatives, in which they showed that these substances might be represented as containing a special group or radical, termed *benzoyl*, which behaved like an element. The idea of groups of elements going in and out of

combination like a simple substance was not new to chemists: there was not only the case of cyanogen, discovered by Gay Lussac in 1815. The attempt had been made by Dumas and Boullay in 1828 to classify the derivatives of alcohol and ether as compounds containing a common radical *etherin*. Gay Lussac had pointed out that the vapour density of ethyl alcohol seemed to show that it consisted of equal volumes of ethylene and water. Robiquet had also shown that ethyl chloride might be assumed to be a compound of hydrochloric acid and ethylene; and Döbereiner had regarded anhydrous oxalic acid as a combination of carbonic acid with carbonic oxide.

But the investigation of Liebig and Wöhler served to give precision to the conception. It thereby exercised a profound influence on the development of organic chemistry by demonstrating, in effect, that this branch of the science might be regarded as the chemistry of the compound radicals, in contradistinction to inorganic chemistry—the chemistry of the simple radicals. Additional support for this view was afforded by the remarkable research by Bunsen on the so-called *alkarsin*, the “fuming liquor of Cadet”—an evil-smelling substance long known as being formed when an acetate is heated with arsenious oxide. Bunsen showed that this liquid contained a compound radical having arsenic as a constituent; and he prepared a series of derivatives, all of which might be formulated as combinations of this radical, which he termed *cacodyl*. The study of the electrolytic decomposition of the acetates by Kolbe and the discovery of *zinc-ethyl* by Frankland afforded powerful support to the doctrine of combined radicals.

Although there can be no doubt that this doctrine greatly stimulated the pursuit of organic chemistry, it

was gradually perceived that to regard inorganic and organic chemistry as the chemistry respectively of the simple and of the compound radicals was an imperfect and misleading conception of the true relations of the two main divisions of the science. Facts showed that the properties of a substance depend more on the arrangement of its atoms than on their nature. The doctrine of compound radicals was implicitly an attempt to extend the dualistic conceptions of Berzelius to the facts of organic chemistry; and as such it was welcomed by the great Swedish chemist. But dualism was found to have its limitations, even in inorganic chemistry; and these were still more apparent when it was sought to apply it in the other main branch of the science. Attempts were therefore made—notably by the French chemists Laurent, Dumas, and Gerhardt—to formulate organic substances by methods in which the electrochemical and dualistic conceptions of Berzelius and his followers had no part. How these attempts developed, and how they subsequently grew into the organic chemistry of to-day, will be shown in the second part of this work.

It will be convenient also to delay any account of the personal history of the creators of the science of organic chemistry—Liebig, Wöhler, Dumas—until we are in a position to give a fuller statement of their labours, and of the results which flowed from them. Although the foundations of organic chemistry may be said to have been laid during the closing years of the first half of the nineteenth century, the superstructure was not erected until the second half.

## CHAPTER XII.

### THE RISE OF PHYSICAL CHEMISTRY

PHYSICS and Chemistry are twin sisters—daughters of Natural Philosophy ; like Juno's swans, coupled and inseparable. Physics is concerned with the forms of energy which affect matter ; chemistry with the study of matter so affected. Each, then, is complementary to the other. Philosophers of old drew no practical distinction between them, at least as regards their own studies. Men like Boyle, Black, Cavendish, Lavoisier, Dalton, Faraday, Graham, Bunsen, were pioneers "on a very broad gauge," pushing their inquiries into territories common to the two branches, as their genius or inclinations directed them. Accordingly, it has happened that many so-called physical laws have been discovered by men who were professed chemists. It has also happened that men who began their scientific career as chemists, like Dalton, Regnault, and Magnus, eventually gave the whole of their energies to physical measurements ; or, like Black, Faraday, and Graham, devoted themselves to the elucidation of physical problems. As certain of these physical laws and problems have greatly influenced the progress of chemistry, it becomes necessary, in any historical treatment of the subject, to give some account of their origin, and to show how they affected the development of chemical theory.

The relations of heat to chemical phenomena are so obvious and so intimate that the study of their connection

necessarily attracted attention in very early times. But it was only when this study became quantitative that any important generalisations became possible. Most quantitative estimations of heat depend eventually upon the thermometer; and thermometry is indebted to Englishmen in the first instance for attempts to render the instrument trustworthy.

In this connection may be mentioned the names of Newton and Shuckburgh. Brooke Taylor, in 1723, made a special study of the mercurial thermometer as a measurer of temperature. In other words, he sought to discover whether equal differences of expansion or contraction of mercury corresponded to equal additions or abstractions of heat. The results showed that the principle of the mercurial thermometer is valid within at least the limits of temperature between the boiling and freezing-points of water. These experiments were subsequently repeated and confirmed by Cavendish, and, independently, by Black.

The discovery of the phenomenon of *latent heat* by Black some time prior to 1760 marks an epoch in the history of science. It was then for the first time clearly recognised that the state of aggregation of a substance is associated with a definite thermal quantity, and that, in order to effect a change, a definite amount of energy, in the form of heat, must be employed. The quantitative connection that exists between work and energy was thus foreshadowed.

The doctrine of *specific heat* was taught by Black in his lectures at Glasgow between 1760 and 1765. The subject was subsequently investigated experimentally by Irvine between 1765 and 1770, and by Crawford in 1779. A series of determinations was published in 1781 by Wilcke, in the *Transactions* of the Swedish

Academy. In these the term *specific caloric*, since changed to *specific heat*, was first used. About this time the determination of the amount of heat required to raise substances through a definite interval of temperature was made the subject of experiment by many observers, notably by Lavoisier and Laplace, who greatly improved the calorimetric arrangements. The values they obtained long remained the most trustworthy estimations of the specific heats of substances. Their joint research had a further influence on the development of thermo-chemistry by indicating the general experimental conditions which were needed to ensure accuracy in such determinations. Lavoisier and Laplace also measured, in 1782–1783, the heat disengaged by the combustion of substances, and that evolved during respiration. In 1819 Dulong and Petit pointed out that the specific heats of a number of substances, more particularly the metals, were inversely proportional to their atomic weights; or, in other words, the product of the specific heat into the atomic weight was a constant. The nature of the relation will be seen from the following table of certain of the results obtained by Dulong and Petit:—

Element.		At. wt.		Spec. heat.		Atomic heat.
Bismuth	...	208	...	0.0288	...	6.0
Lead	...	207	...	0.0293	...	6.0
Gold	...	197	...	0.0298	...	5.8
Platinum	...	195	...	0.0314	...	6.1
Silver	...	108	...	0.0570	...	6.1
Copper	...	63	...	0.0952	...	6.0
Iron	...	56	...	0.1138	...	6.4

It will be seen that these various elements have an uniform, or nearly uniform, atomic heat—approximately 6.2 on the average.

This would appear to prove that, as Dulong and Petit expressed it, “the atoms of simple substances



have equal capacities for heat." The variations from a constant value are due partly to errors of observation, but more particularly to the circumstance that the substances compared are not all in a strictly comparable condition—*e.g.*, they are not all equally remote from their melting points. It was shown, moreover, that the amount of heat needed to raise a substance through a definite interval of temperature increased with the temperature. The range of temperature through which a determination was made in a particular instance affected, therefore, the value of the specific heat. The most noteworthy departures from a uniform value were observed to occur among the metalloids—*e.g.*, carbon, the various modifications of which had different specific heats—and generally among elements of low atomic weight, in which the variation of specific heat with temperature was particularly rapid.

Nevertheless, the significance of the generalisation discovered by Dulong and Petit, in spite of its limitations, was quickly appreciated, as it was perceived that a knowledge of the specific heat of an element might be of great value in determining its atomic weight. The immediate effect was that a certain number of the atomic weights fixed by Berzelius mainly on chemical considerations were required to be halved. Although subsequent experience has proved that the law of Dulong and Petit is not capable of the simple mathematical expression they gave it, it has shown itself to be of great value in fixing doubtful atomic weights.

**Pierre Louis Dulong** was born in 1785 at Rouen, and, after studying chemistry and physics at the Polytechnic School at Paris, became its Professor of Chemistry and subsequently its Professor of Physics. In 1830

he was made its Director of Studies; and in 1832 he became permanent Secretary of the Academy of Sciences. As a young man he worked with Berzelius, with whom he made the first approximately accurate determination of the gravimetric composition of water. In 1811 he discovered the highly explosive *nitrogen chloride*, in the investigation of which he was severely injured, losing an eye and several fingers. He died in 1838. His collaborator, **Alexis Therese Petit**, was born in 1791 at Vesoul, and died, when holding the position of Professor of Physics at the Lycée Bonaparte, in 1820.

The attempt made by Neumann to extend Dulong and Petit's "law" to compound substances was only partially successful. Nor has any important generalisation followed from our knowledge of the specific heat of liquids. Almost simultaneously with the publication of Dulong and Petit's "law," Mitscherlich made known the fact that similarity in chemical constitution is frequently accompanied by identity of crystalline form. Boyle, as far back as the middle of the seventeenth century, had insisted upon the importance of the forms of crystals in throwing light upon the internal structure of bodies. Romé de l'Isle and Haüy had remarked that many different substances had the same crystalline form. It had been observed that a crystal of potash alum would continue to grow and preserve its shape in a solution of ammonia alum; and similar observations had been shown to occur in the case of vitriols. The invention of the reflecting goniometer by Wollaston greatly facilitated the investigation of such phenomena. Mitscherlich showed that the phosphates and arseniates of analogous composition had the same crystalline shape, or, in other words, were isomorphous. The same fact was observed to occur in the case of the analogously

constituted sulphates and selenates, and in that of the oxides of magnesium and zinc, etc'. The value of isomorphous relations in determining the group-relationships of the elements and in deducing the composition of salts was at once recognised by Berzelius, who styled the discovery of isomorphism by his pupil Mitscherlich as "the most important since the establishment of the doctrine of chemical proportions." The quantities of the isomorphously replacing elements in a compound were regarded by him as a measure of their atomic weights; and the principle was subsequently constantly employed by him, whenever possible, as a criterion in fixing their values. Other investigators have followed his example in this respect; and isomorphism is still regarded as an important consideration in establishing the genetic relations of an element.

**Eilhard Mitscherlich**, the son of a minister, was born in 1794 at Neu Ende, near Jever, in Oldenburg, and, after studying philology and oriental languages at Heidelberg, went to Paris, and thence to Göttingen, where he occupied himself with natural science. In 1818 he repaired to Berlin and commenced to work on the arseniates and phosphates, the similarity in the crystal-forms of which he was the first to detect. His friend Gustav Rose, the mineralogist, thereupon instructed him in the methods of crystallography, to enable him to verify his discovery and to establish it by goniometric measurements. In 1821 he joined Berzelius at Stockholm, where he pursued his inquiries on the connection between crystal-form and chemical composition. It was at the suggestion of Berzelius that he adopted the term "isomorphy" to express this connection—the mechanical consequence of identity of atomic constitution. In the same year

he was appointed Klaproth's successor in Berlin, where he died in 1863.

Mitscherlich also worked on the manganates and permanganates, on selenic acid, on benzene and its derivatives, and on the artificial production of minerals.

The study of the physical phenomena of gases, initiated in 1660 by Boyle's discovery of the law of gaseous pressure, has greatly contributed to our knowledge of their intrinsic nature. Boyle himself only proved his law in the case of atmospheric air; but the observation was subsequently (1676) generalised by Marriotte. Charles, Dalton, and Gay Lussac independently showed that gases have the same rate of thermal expansion.

That gases are made up of particles possessing an internal movement was surmised by the Greeks; but experimental evidence for such a view of their constitution was first presented by Thomas Graham in 1829-1831, when he discovered that gases move, or are diffused, at rates inversely proportional to the square roots of their densities. Observations of a like character, which found their explanation in Graham's discovery, had previously been made by Priestley, Dohereiner, and Saussure. This interchange in the position of their particles is a property inherent in gases. Inequality of density is not essential to diffusion. Graham proved this by connecting together two vessels, one containing nitrogen and the other carbonic oxide, which have the same density. After the expiration of a certain time both gases were found to be uniformly diffused through the vessels.

How these laws were found to be interdependent and mutually connected, and how they led up to a molecular theory of gases which serves to explain them, as well as certain other gaseous phenomena to be

subsequently noted, will be shown in the second part of this work.

By the end of the period with which we are concerned—that is, the middle of the nineteenth century—a considerable body of information had been accumulated as to the conditions which determine the different states of aggregation of matter—that is, the conditions which allow of the passage of the gaseous state into that of the liquid, and of the liquid into that of the solid. That the same substance was capable of existence in the three states of gas, liquid, and solid was of course evident from the case of water. Even the most primitive races must have realised that steam, dew, rain, snow, hail, and ice were only modifications of one and the same substance. As knowledge increased, other substances came to be known which resembled water in their capacity for existence in various physical states. It was but natural to assume that this was a general attribute, and that all substances would, sooner or later, be found capable of existence in each of the different conditions of aggregation.

Attempts were made during the first quarter of the last century to prove that all the æriform bodies then known were simply vapours more or less remote from their point of liquefaction, and still further removed from their point of congelation. Monge and Clouet condensed sulphur dioxide some time before 1800; and Northmore, in 1805, liquefied chlorine. But these observations attracted little attention until Faraday, in 1823, independently effected the liquefaction of chlorine, and Davy that of hydrochloric acid. Faraday almost immediately afterwards liquefied sulphur dioxide, sulphuretted hydrogen, carbon dioxide, euchlorine, nitrous oxide, cyanogen, and ammonia.

Other experimenters, among whom may be mentioned Thilorier and Natterer, greatly improved the mechanical appliances for liquefying these gases; liquid carbonic acid and nitrous oxide were obtained in considerable quantities, and employed in the production of cold. Certain of the gases—hydrogen, oxygen, nitrogen, nitric oxide, carbonic oxide, etc.—resisted all attempts to liquefy them; and hence gaseous substances came to be classified as *permanent* and *non-permanent*, depending upon whether they could or could not be liquefied. The division was felt to be irrational even at the time it was made. There seemed no *à priori* reason why carbon dioxide and nitrous oxide should be liquefiable, while carbonic oxide and nitric oxide should resist all attempts to coerce them into changing their state. The real clue to the conditions required to effect the liquefaction of a gas was not discovered until nearly half a century later, when, as will be shown subsequently, the arbitrary division of gases into permanent and non-permanent was swept away.

The discovery of the law of gaseous combination by Gay Lussac, and the recognition by Ampère and Avogadro of the relation between the density of a gas or a vapour and its atomic weight, early led to improvements in the methods of determining the absolute weights of gases and vapours, especially by French chemists. Both Gay Lussac and Dumas devised processes for determining vapour densities which were in use until late in the century, and which, although now superseded by more convenient and more rapid modifications, afforded valuable information concerning the molecular weights of substances and the phenomena of gaseous dissociation.

During the first decade of the nineteenth century

Dalton and Henry discovered the simple law which connects pressure with the solubility of a gas in any solvent upon which it exerts no specific action. Dalton further developed the law so as to include the absorption by a solvent of the several constituents of a gaseous mixture.

Attempts were made by Schröder, Kopp, and others, to discover relations between the weights of unit volumes of liquids and solids and their chemical nature; but such attempts were only partially successful, owing to the difficulty of finding valid conditions of comparison. By comparing the specific gravities of liquids at their boiling-points Kopp succeeded in detecting a number of regularities among their specific volumes which seem to indicate that a comprehensive generalisation connecting them may yet be discovered. Kopp has also shown that regularities exist among the boiling-points of correlated substances, and that there is an interdependence between the temperature of their ebullition and the chemical characters of compounds.

This short summary will suffice to show that attempts to discover relations between the physical attributes of substances and their chemical nature were made more or less sporadically from the time that chemistry was pursued in the spirit of science. But it is only in recent times that any great accession to knowledge has resulted from such efforts. The science of physical chemistry is practically a creation of our own period. Its systematic study may be said to date only from the last quarter of the nineteenth century, since which time it has made extraordinary progress. Its broad features will be dealt with in the second volume of this work.

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JUSTUS VON LIEBIG.

# HISTORY OF CHEMISTRY

BY

SIR EDWARD THORPE,  
C.B., LL.D., F.R.S.

AUTHOR OF "ESSAYS IN HISTORICAL CHEMISTRY," "HUMPHRY DAVY:  
POET AND PHILOSOPHER," "JOSEPH PRIESTLEY," ETC., ETC.

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## CHAPTER I.

### STATE OF CHEMISTRY IN THE MIDDLE OF THE NINETEENTH CENTURY

IN the preceding volume an attempt was made to outline the significant features in the development of chemistry, as an art and as a science, from the earliest times down to about the middle of the last century. Since that time chemistry has progressed at a rate and to an extent unparalleled at any period of its history. Not only have the number and variety of chemical products—inorganic and organic—been enormously increased, but the study of their modes of origin, properties, and relations has greatly extended our means of gaining an insight into the internal structure and constitution of bodies. This extraordinary development has carried the science beyond the limits of its own special field of inquiry, and has influenced every department of natural knowledge. Concurrently there has been a no less striking extension of its applications to the prosperity and material welfare of mankind.

With the death of Davy the era of brilliant discovery in chemistry, wrote Edward Turner, appeared for the moment to have terminated. Although the number of workers in the science steadily increased, the output of chemical literature in England actually diminished for some years; and, as regards inorganic chemistry, few first-rate discoveries were made during the two decades prior to 1850. Chemists seemed to be of Turner's

opinion that the time had arrived for reviewing their stock of information, and for submitting the principal facts and fundamental doctrines to the severest scrutiny. Their activity was employed not so much in searching for new compounds or new elements as in examining those already discovered. The foundations of the atomic theory were being securely laid. The ratios in which the elements of known compounds are united were being more exactly ascertained. The efforts of workers, Graham excepted, seemed to be spent more on points of detail, on the filling-in of little gaps in the chemical structure, as it then existed, than in attempts at new developments. For a time—during the early 'thirties—chemists struggled with the claims of rival methods of notation, and it was only gradually that the system of Berzelius gained general acceptance. At none of the British universities was there anything in the nature of practical tuition in chemistry. Thomson, at Glasgow, occasionally permitted a student to work under him, but no systematic instruction was ever attempted. The first impulses came from Graham in 1837, when he took charge of the chemical teaching at the University of London, and when, in 1841, he assisted to create the Chemical Society of London. Four years later the Royal College of Chemistry in London was founded and placed under the direction of **August Wilhelm, Hofmann**—one of the most distinguished pupils of Liebig. Under his inspiration the study of practical chemistry made extraordinary progress, and discovery succeeded discovery in rapid succession. In bringing Hofmann to England we had, in fact, imported something of the spirit and power of his master, Liebig.

Among the pupils and co-workers of Hofmann were

Warren de la Rue, Abel, Nicholson, Mansfield, Medlock, Crookes, Church, Griess, Martius, Sell, Divers, and Perkin. Whilst at Giessen he had begun the study of the organic bases in coal-tar with a view more especially of establishing the identity of Fritzsche's *anilin* with the *benzidam* of Zinin and the *krystallin* of Unverdorben. Hofmann continued to cultivate with unremitting zeal the field thus entered. With Muspratt he discovered *paratoluidine* and *nitraniline*; with Cahours *allyl alcohol*. His pupil Mansfield worked out, at the cost of his life, the methods for the technical extraction of benzene and toluene from coal-tar, and thereby made the coal-tar colour-industry possible. It was in attempting to synthesise quinine by the oxidation of aniline that Perkin, then an assistant at the college, obtained, in 1856, *aniline purple*, or *mauve*, as it came to be called by the French, the first of the so-called coal-tar colouring matters. In 1859 this was followed by the discovery of *magenta*, or *fuchsine*, by Verquin. For its manufacture Medlock, one of Hofmann's pupils, in 1860 devised a process by which for a time it was almost exclusively made. Hofmann studied the products thus obtained, and showed that they were derivatives of a base he called *rosaniline*; and he demonstrated that the colouring matters were only produced through the concurrent presence of aniline and toluidine. He also proved that the base of the dye, known as *aniline blue*, was *triphenylrosaniline*. As the result of these inquiries he obtained the violet or purple colouring matters known by his name. Lastly, all his classical work on the amines, ammonium compounds, and the analogous phosphorus derivatives was done at the Royal College of Chemistry.

Prior to the establishment by Liebig, in 1826, of the



Giessen laboratory, the state of chemistry in Germany was not much, if at all, better than with us. The creation of the Giessen school initiated a movement which has culminated in the pre-eminent position which Germany now occupies in the chemical world. Students from every civilised country came to study and to work under its leader, and to carry away with them the influence of his example, the inspiration of his genius, and the stimulating power of his enthusiasm.

**Justus von Liebig** was born at Darmstadt on May 12th, 1803, and after graduating at Erlangen, where he worked on the fulminates, he repaired to Paris and entered the laboratory of Gay Lussac, with whom he continued his inquiries. Returning to Germany, he was appointed Professor of Chemistry at Giessen in 1826, and began those remarkable series of scientific contributions upon which the superstructure of organic chemistry largely rests. He investigated the *cyanates*, *cyanides*, *ferrocyanides*, *thiocyanates*, and their derivatives. In conjunction with Wöhler he discovered the group of the *benzoic compounds* and created the *radical theory*. With Wöhler also he investigated *uric acid and its derivatives*. He discovered *hippuric acid*, *fulminuric acid*, *chloral*, *chloroform*, *aldehyde*, *thialdine*, *benzil*, and elucidated the *constitution of the organic acids* and the *amides*. He greatly improved the methods of organic analysis, and was thereby enabled to determine the empirical formulæ of a number of carbon compounds of which the composition was imperfectly known. He practically laid the foundations of modern agricultural chemistry, and to his teaching is due the establishment of an important branch of technology—the manufacture of chemical fertilisers. He worked on physiological chemistry, especially on the elaboration

of fat, on the nature of blood, bile, and on the juice of flesh. He studied the processes of fermentation, and of the decay of organised matter. He was a most prolific writer. The Royal Society's Catalogue of Scientific Papers enumerates no fewer than 317 contributions from his pen. He was the founder of the *Annalen der Chemie*, which is now associated with his name, and of the "Jahresbericht"; he published an encyclopædia of Pure and Applied Chemistry and a Handbook of Organic Chemistry. His "Familiar Letters on Chemistry" was translated into every modern language, and exercised a powerful influence in developing popular appreciation of the value and utility of science. Liebig left Giessen in 1852 to become Professor of Chemistry at the University of Munich and President of the Academy of Sciences. He died at Munich on April 18th, 1874.

With the name of Liebig that of Wöhler is indissolubly connected. Although the greater part of their work was not published in conjunction, what they did together exercised a profound influence on the development of chemical theory.

**Friedrich Wöhler** was born at Eschersheim, near Frankfort, on July 31st, 1800. After studying at Marburg, where he discovered, independently of Davy, *cyanogen iodide*, and worked on *mercuric thiocyanate*, he went to Heidelberg and investigated *cyanic acid* and its compounds, under the direction of Gmelin. In 1823 he worked with Berzelius at Stockholm, where he prepared some new tungsten compounds and practised mineral analysis. In 1825 he became a teacher of chemistry in the Berlin Trade School. Here he succeeded for the first time in preparing the metal *aluminium* and in effecting the *synthesis of urea*—one

of the first organic compounds to be prepared from inorganic materials. Jointly with Liebig he worked upon *mellitic* and *cyanic* and *cyanuric acids*. In 1832 Wöhler, now appointed to the Polytechnic at Cassel, began with Liebig their memorable investigation on *bitter almond oil*. In 1836 he was called to the chair of chemistry in the University of Göttingen, and with Liebig attacked the constitution of *uric acid and its derivatives*—the last great investigation the friends did in common. Wöhler subsequently devoted himself mainly to inorganic chemistry. He isolated *crystalline boron*, and prepared its *nitrides*, discovered the spontaneously inflammable *silicon hydride*, *titanium nitride*, and analysed great numbers of minerals and meteorites and compounds of the rarer metals. He made Göttingen famous as a school of chemistry. At the time of the one and twentieth year of his connection with the University it was found that upwards of 8,000 students had listened to his lectures or worked in his laboratory. He died on September 23rd, 1882.

In France Dumas exercised a no less powerful influence. If Liebig could reckon among his pupils Redtenbacher, Bromeis, Varrentrapp, Gregory, Playfair, Williamson, Gilbert, Brodie, Anderson, Gladstone, Hofmann, Will, and Fresenius; Dumas could point to Boullay, Piria, Stas, Melsens, Wurtz, and Leblanc—all of whom did yeoman service in developing the rapidly expanding branch of organic chemistry.

**Jean Baptiste André Dumas** was born on July 14th, 1800, at Alais, where he was apprenticed to an apothecary. In his sixteenth year he went to Geneva and entered the pharmaceutical laboratory of Le Royer. Without, apparently, having received any systematic instruction in chemistry, he commenced the work of



JEAN BAPTISTE ANDRÉ DUMAS.

investigation. With Coindet he established the therapeutic value of iodine in the treatment of *goître*; with Prevost he attempted to isolate the active principle of *digitalis*, and studied the chemical changes in the development of the chick in the egg. In his twenty-fourth year Dumas went to Paris and became *Répétiteur de Chimie* at the Ecole Polytechnique. He joined Audouin and Brongniart in founding the *Annales des Sciences Naturelles*, and began his great work on Chemistry Applied to the Arts, of which the first volume appeared in 1828. At about this time he devised his *method of determining vapour densities*, and published the results of a number of estimations made by means of it. With Boullay he began an inquiry on the *compound ethers*, out of which grew the *etherin theory*, which served as a stepping-stone to the theory of compound radicals—subsequently elaborated by\*Liebig and Wöhler. Dumas discovered the nature of *oxamide* and of *ethyl oxamate*, isolated *methyl alcohol*, and established the generic connection of groups of similarly constituted organic substances, or, in a word, the doctrine of *homology*. His work on the *metaleptic action of chlorine* upon organic substances eventually effected the overthrow of the electro-chemical theory of Berzelius and led to the theory of types, which, in the hands of Williamson, Laurent, Gerhardt, and Odling, was of great service in explaining the analogies and relationships of whole groups of organic compounds. He worked in every field of chemistry. He invented many analytical processes, established the *gravimetric composition of water and of air*, and revised the *atomic weights* of the greater number of the elements then known. Dumas exercised great influence in scientific and academic circles in France. He was an

admirable speaker, and had rare literary gifts. On the creation of the Empire he was made a Senator, and was elected a member of the Municipal Council of Paris, of which he became president in 1859. He died on April 11th, 1884.

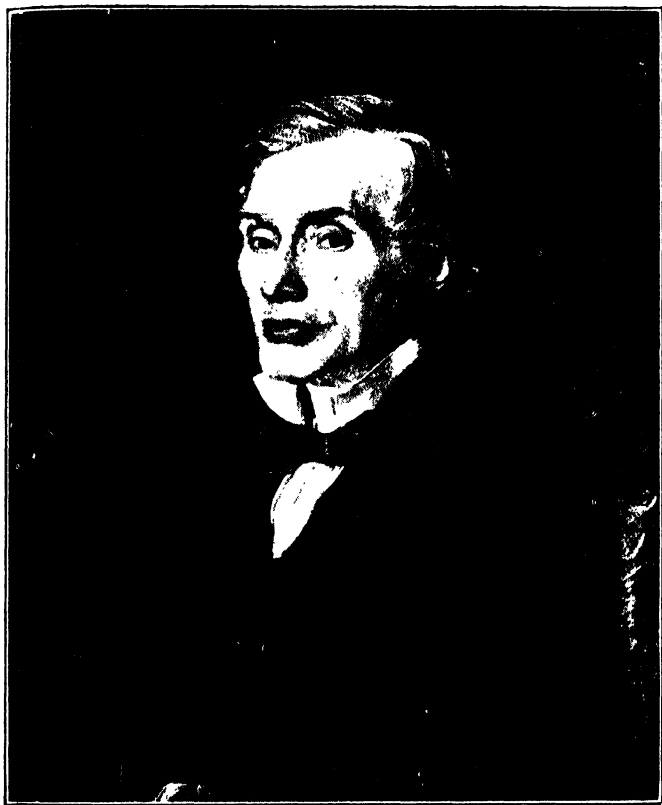
It was largely through the influence of these master-minds that chemistry took a new departure. Prior to their time organic chemistry hardly existed as a branch of science: organic products, as a rule, were interesting only to the pharmacist mainly by reason of their technical or medicinal importance. But by the middle of the nineteenth century the richness of this hitherto untilled field became manifest, and scores of workers hastened to sow and to reap in it. The most striking feature, indeed, of the history of chemistry during the past sixty years has been the extraordinary expansion of the organic section of the science. The chemical literature relating to the compounds of carbon now exceeds in volume that devoted to all the rest of the elements.

In the middle of the nineteenth century chemists began to concern themselves with the systematisation of the results of the study of organic compounds, and something like a theory of organic chemistry gradually took shape. From this period we may date the attempts at expressing the internal nature, constitution, and relations of substances which, step by step, have culminated in our present representations of the structure and spatial arrangement of molecules. In 1850 the dualistic conceptions of Berzelius ceased to influence the doctrines of organic chemistry. The enunciation by Dumas of the principle of substitution, and its logical outcome in the nucleus theory and in the theory of types, had not only effected the overthrow of

dualism, but was undermining the position of the radical theory of Liebig and Wöhler. The teaching of Gerhardt and Laurent had spread over Europe, and was influencing those younger chemists who, while renouncing dualism, were not wholly satisfied with a belief in compound radicals. Williamson's discovery, in 1850, of the true nature of ether and of its relation to alcohol, and his subsequent preparation of mixed ethers, served not only to reconcile conflicting interpretations of the process of etherification, but also to reconcile the theory of types with that of radicals. Lastly, his method of representing the constitution of the ethers and their mode of origin gave a powerful stimulus to the use of type-formulæ in expressing the nature and relations of organic compounds.

Other representative men of the middle period of the nineteenth century, in addition to Williamson, were Graham and Bunsen. The three men were investigators of very different type, and their work had little in common. But each was identified with discoveries of a fundamental character, constituting turning-points in the history of chemical progress, valuable either as regards their bearing on chemical doctrine or as regards their influence on operative chemistry.

**Thomas Graham** was born in Glasgow on December 21st, 1805, and, after studying under Thomas Thomson at the University of that city, attended the lectures of Hope and Leslie in Edinburgh. In 1830 he succeeded Ure as teacher of chemistry at Anderson's College in Glasgow, and in 1837 was called to the chair of chemistry in the newly-founded University of London, in succession to Edward Turner. In 1854 he was made Master of the Mint. He died in London on September 16th, 1869.



THOMAS GRAHAM.

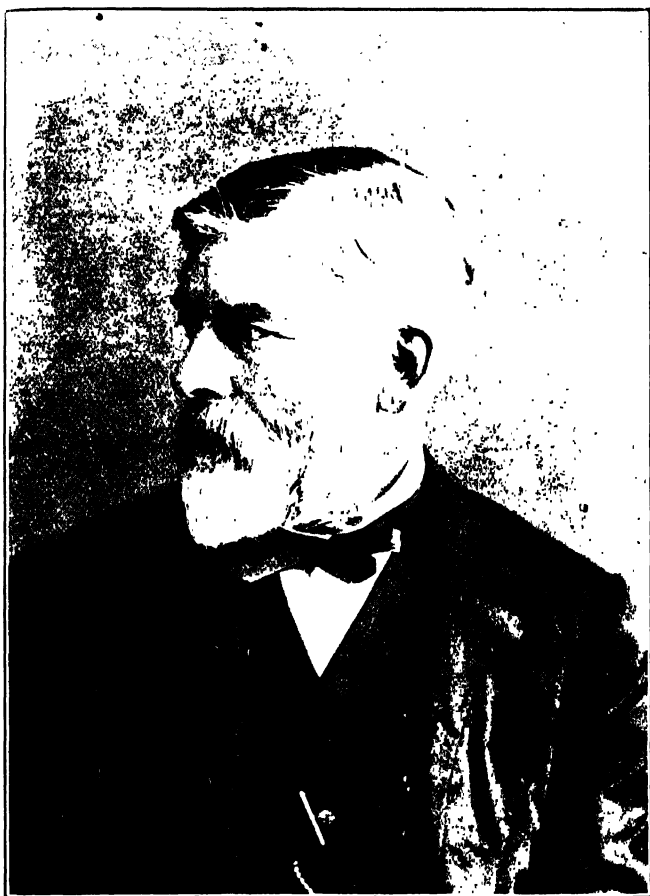
From a painting by G. F. Watts, R.A., in the possession of the Royal Society.



Graham's work was mainly devoted to that section of the science now known as physical chemistry. His contributions to pure chemistry are few in number. By far the most important is his discovery of *meta-phosphoric* acid and its relations to the other modifications of phosphoric acid. Ortho- or ordinary phosphoric acid was known to Boyle; pyrophosphoric acid was discovered by Clark. Graham's work is noteworthy as first definitely indicating the inherent property of the acids to combine with variable but definite amounts of basic substances by successive replacement of hydroxyl groups—the property we now term *basicity*, and was of fundamental importance in regard to its bearing on the constitution of acids and salts.

Graham's fame chiefly rests upon his discovery of the *law of gaseous diffusion* (1829-1831), upon his work on the *diffusion of liquids*, and upon his recognition of the condensed form of hydrogen he termed *hydrogenium*. Questions involving the conception of molecular mobility, indeed, constituted the main feature of his inquiries. We owe to him, among others, the terms *crystalloid*, *colloid*, *dialysis*, *atmolysis*, *occlusion*—all of which have taken a permanent place in the terminology of science.

**Alexander William Williamson** was born at Wandsworth, London, on May 1st, 1824. His father, a Scotchman and a fellow-clerk of James Mill (the father of John Stuart Mill) in the East India House, took an active share in the foundation, in 1826, of the University of London, subsequently known as University College. In 1840 the younger Williamson entered the University of Heidelberg with the intention of studying medicine; but, under the influence of Leopold Gmelin, he turned to chemistry. In 1844 he



ALEXANDER WILLIAM WILLIAMSON.

went to Giessen, to work under Liebig, and there made his first contributions to chemical science—viz., on the *decomposition of oxides and salts by chlorine*; on *ozone*; and on the *blue compounds of cyanogen and iron*. After graduating at Giessen he went, in 1846, to Paris, where he came under the influence of Comte, with whom he studied mathematics. In 1850, at Graham's solicitation, he was appointed to the Chair of Practical Chemistry at University College, vacant by the death of Fownes. He at once embarked upon those researches which constitute his main contribution to science. In the attempt to build up the homologous series of the aliphatic alcohols from ordinary alcohol he succeeded in demonstrating the real nature of ether and its genetic relation to alcohol, and in explaining the process of etherification. The memoirs (1850-52) in which he embodied the facts had an immediate influence on the development of chemical theory. His explanation of the process of etherification familiarised chemists with the idea of the essentially dynamical nature of chemical change. He imported the conception of molecular mobility not only into the explanation of such metathetical reactions as the formation of the ethers, but into the interpretation of the phenomena of chemical change in general. In these papers, as also in one on the constitution of salts, published in 1851, he attempted to systematise the representation of the constitution and relations of oxidised substances—organic and inorganic—by showing how they may be regarded as built up upon the type of water considered as  $\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \text{O}$ , in which the hydrogen atoms are replaced, wholly or in part, by other chemically equivalent atoms. This idea was immediately adopted by Gerhardt, was

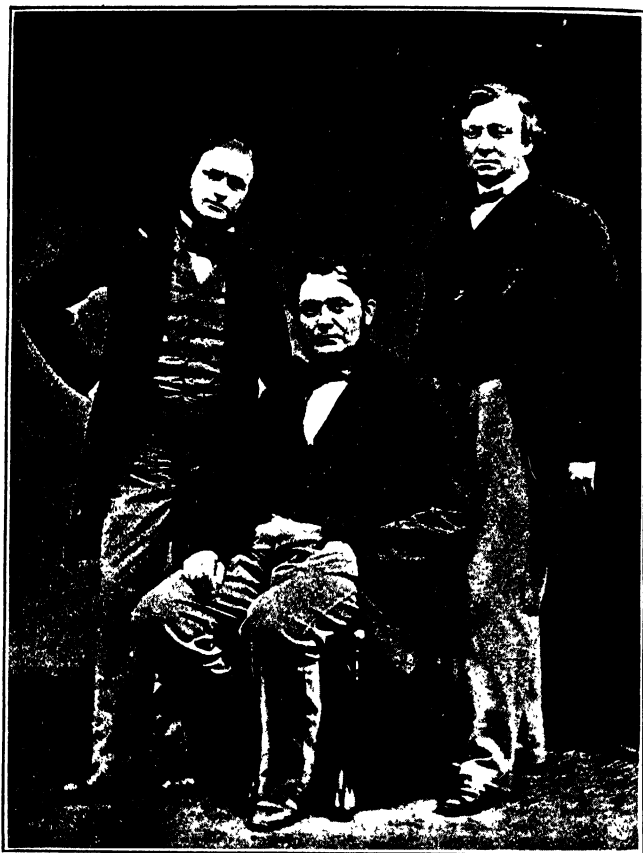
further elaborated by Odling and Kekulé, and was eventually developed into a theory of chemistry.

Williamson continued to direct the laboratory of University College until 1887, when he retired to the country. He died at Hindhead on May 6th, 1904.

**Robert Wilhelm Bunsen** was born at Göttingen on March 31st, 1811, and after studying chemistry under Stromeyer, the discoverer of cadmium, went to Paris and worked with Gay Lussac. In 1836 he succeeded Wöhler as teacher of chemistry in the Polytechnic School of Cassel, and in 1842 became professor of chemistry in the University of Marburg. In 1852 he was called to Heidelberg, and occupied the chair of chemistry there until his retirement in 1889. He died at Heidelberg on August 16th, 1899.

Bunsen first distinguished himself by his classical work on the *cacodyl compounds*, obtained as the result of an inquiry into the nature of the so-called "fuming liquor of Cadet," an evil-smelling, highly poisonous, inflammable liquid formed by heating arsenious oxide with an alkaline acetate. The investigation (1837-1845) is noteworthy, not only for the skill it exhibits in dealing with a difficult and highly dangerous manipulative problem, but also for the remarkable nature of its results and on account of their influence on contemporary chemical theory. The research, in the words of Berzelius, was the foundation-stone of the theory of compound radicals. The name *cacodyl* or *kukodyl* was suggested by Berzelius in allusion to the nauseous smell of the compounds of the new radical *arsine-dimethyl*,  $As(CH_3)_2$ , as it was subsequently termed by Kolbe.

Bunsen greatly improved the methods of gasometric analysis; these he applied, in conjunction with Playfair,



BUNSEN, KIRCHHOFF, AND ROSCOE.

to an examination of the gaseous products of the blast furnace in the manufacture of iron, and thereby demonstrated the enormous waste of energy occasioned by allowing the gases to escape unused into the air, as was then the universal practice. This inquiry effected a revolution in the manufacture of iron as important, indeed, as that due to the introduction of the hot blast.

Bunsen devised methods for determining the *solubility of gases* in liquids, for ascertaining the *specific gravity of gases*, their *rates of diffusion*, and of combination or *inflammation*. In 1841 he invented the *carbon-zinc battery*, and applied it to the electrolytic production of metals, notably of *magnesium*, the properties of which he first accurately described. In 1844 he contrived the *grease-spot photo-meter*, which was long in general use for ascertaining the photometric value of illuminating gas. His methods of ascertaining *the specific heats of solids and liquids* were simple, ingenious, and accurate. In 1855-1863 he carried out, in conjunction with Roscoe, a long series of investigations on the *chemical action of light*. In 1859, in association with Kirchhoff, he devised the first methods of *spectrum analysis*, and explained the origin and significance of the Fraunhofer lines in the solar spectrum, thus laying the foundations of solar and stellar chemistry. The application of the *spectroscope* to analytical chemistry almost immediately resulted in his discovery of *cæsium* and *rubidium*.

Bunsen worked on problems of *chemical geology*, and made a long series of analyses of *volcanic products*. With Schischkoff, he examined, in 1857, the products of fired gunpowder. He effected many improvements in analytical chemistry; devised the *iodimetric method* of volumetric analysis, and systematised the processes of *water analysis*. Lastly, he invented the *gas-burner*

—a piece of apparatus with which his name is inseparably associated, and which has been of inestimable service to operative chemistry and in the arts. Bunsen was no theorist, and purely speculative questions had little or no interest for him. At the same time he was a great teacher, and made the chemical school of Heidelberg no less famous than the schools of Giessen and Göttingen.

The mass of material relating to the development of chemistry which has been accumulated during the past sixty years is so vast that it would be hopeless to attempt to survey it in detail within the limits of such a work as this. Nor, indeed, is this required in a history of this character. Those who desire information concerning the origin and sequence of the facts which collectively make up the superstructure of modern chemistry must be referred to the encyclopædias or larger treatises—or, preferably, to the numerous monographs, dealing with special sections, which the volume and complexity of the matter to be dealt with seem to render increasingly necessary. All we can do here is to attempt to show what has been the main outcome of this sixty years of incessant effort to elucidate the mysteries of chemical phenomena and to ascertain the nature of the conditions which control, modify, or determine them. All this effort is ultimately directed to the solution of the fundamental problem of the constitution of matter. The most significant result of this endeavour has been the elaboration and consolidation of the doctrine of chemical atoms, not necessarily of atoms in the limited Daltonian sense, but of atoms considered as associations of particles, or corpuscles—that is, of entities

which *may* be divisible, but which, in the main, are not divided in the vast number of the transformations in which they are concerned. This modification of the original conception of Dalton has been thought by some to destroy the basis upon which his theory really rests. There is no necessity for such an assumption. So pronounced an atomist as Graham, as far back as 1863, in a suggestive paper entitled *Speculative Ideas on the Constitution of Matter*, enlarged the conception of the Daltonian atom in precisely the sense which recent experimental work appears to require. The present position, too, as it affects chemists, was equally well stated by Kekulé in 1867 in the following terms:—

The question whether atoms exist or not has but little significance from a chemical point ; its discussion belongs rather to metaphysics. In chemistry we have only to decide whether the assumption of atoms is an hypothesis adapted to the explanation of chemical phenomena. More especially have we to consider the question whether a further development of the atomic hypothesis promises to advance our knowledge of the mechanism of chemical phenomena.

I have no hesitation in saying that, from a philosophical point of view, I do not believe in the actual existence of atoms, taking the word in its literal signification of indivisible particles of matter ; I rather expect that we shall some day find for what we now call atoms a mathematico-mechanical explanation which will render an account of atomic weight, of atomicity, and of numerous other properties of the so-called atoms. As a chemist, however, I regard the assumption of atoms not only as advisable, but as absolutely necessary, in chemistry. I will even go further, and declare my belief that *chemical atoms exist*, provided the term be understood to denote those particles of matter which undergo no further division in chemical metamorphoses. Should the progress of



science lead to a theory of the constitution of chemical atoms—important as such a knowledge might be for the general philosophy of matter—it would make but little alteration in chemistry itself. The chemical atoms will always remain the chemical unit; and for the specially chemical considerations we may always start from the constitution of atoms, and avail ourselves of the simplified expression thus obtained—that is to say, of the atomic hypothesis. We may, in fact, adopt the view of Dumas and of Faraday—that, *whether matter be atomic or not, thus much is certain: that, granting it to be atomic, it would appear as it now does.*<sup>1</sup>

The greater part of that which follows will be devoted, therefore, to an exposition of certain of the great advances in knowledge—many of them of primary importance—which have been made during the last fifty or sixty years, and which have served to strengthen this extended conception of the atomic theory, and to establish its position as an article of the scientific faith of the twentieth century.

<sup>1</sup> *The Study of Chemical Composition*, by Ida Freund (Cambridge University Press), 1904.

## CHAPTER II.

### THE CHEMICAL ELEMENTS DISCOVERED SINCE 1850

IN 1850 the number of substances generally recognised as chemical elements, in the sense in which that term was first employed by Boyle, was sixty-two. Two members—viz., the *pelopium* of Rose and the *ilmenium* of Hermann—were, however, subsequently shown to be identical with metals already known. At the present time (1910) the number of the chemical elements definitely recognised as such is eighty-two. In 1850, as now, they were broadly classified as metals and non-metals, although it was felt then, no less strongly than now, that no very clear line of demarcation was traceable between the two groups. Sixty years ago the elements usually styled non-metals were thirteen in number; to-day the number is nineteen—the increase being due to the inclusion of arsenic and the discovery of the so-called inactive elements, helium, argon, krypton, neon, and xenon. In 1850 there were forty-seven elements definitely classed as metals; in 1910 the number is sixty-three.

At all periods in the history of chemistry as a science the general tendency has been to name substances, whenever possible, in accordance with the theoretical conceptions of the time, and hence it has happened that the same body at successive periods has had very dissimilar names. But in naming the substances we

term elements, theoretical conceptions are not usually applicable. Oxygen, it is true, derives its name from such a conception; and, etymologically, the name connotes an error. Hydrogen, too, has no more right to be called the *water former* than oxygen. Davy, who invented the term chlorine, advocated that the chemical elements should be named from some distinguishing peculiarity, either of origin or of physical property. In the main this principle has been adopted, especially in later years, although there are numerous instances of names derived from purely arbitrary sources. It is largely for the reason that the names of the elements are, with rare exceptions, unconnected with theories that they have remained unchanged, whereas names of compounds, which are far more frequently dependent upon speculative ideas, have constantly been altered in order to comply with the prevailing hypotheses of the period. At the same time it is not always clear that the etymology of certain of the elements is well ascertained. It has been recently shown, for example, that the commonly accepted origin of the word "antimony" from *antimoine*, based on the alleged experiences of mediæval ecclesiastics, has no valid foundation. The word is, in reality, derived from the Arabic *alhmoud*: this became latinised to *althimodium* and eventually to *antimonium*.

By the middle of the nineteenth century the system of symbolical notation suggested by Berzelius was everywhere current; and, stripped largely of its dualistic associations, this system still remains the most generally convenient method of expressing the composition, analogies, and numerical relations of substances. During the middle of the last century philosophic chemists, although subscribing, with hardly

an exception, to the doctrine of definite combining proportions, were by no means agreed as to the sufficiency of Dalton's explanation of the experimental laws of chemical combination; and the hypothesis of atoms in the Daltonian sense was not universally accepted. To some the atomic theory of Dalton, which assumed that the combining proportion was identical with the relative weight of the atom, was unnecessary as an explanation of the laws of combination. Or at most it was only one out of a variety of molecular conditions in which matter might exist. Consequently some chemists were in the habit of drawing a distinction between *chemical* atoms and *physical* atoms. The chemical atom was identical with the Daltonian atom, but this was by no means the same as the physical atom of Democritus or Leucippus. The view in 1850, in fact, was not very dissimilar from that to which recent experimental inquiry has led. But it can hardly be said that the doubts were dependent upon valid experimental evidence; they arose rather from the erroneous interpretation of imperfectly ascertained facts—upon the supposed inconsistencies of the law of Gay Lussac with the hypotheses of Avogadro and Ampère. As soon as the facts were clearly perceived and the inconsistencies reconciled we heard less of the supposed distinction between the chemical and the physical atom. It is only within quite recent time, and as the result of entirely new lines of inquiry, that the distinction has been revived.

In the early part of the last century attempts were made by Berzelius to classify the chemical elements according to their electro-chemical relations, and by Thomson according as they were "supporters" or "non-supporters of combustion." It was soon perceived

that Thomson's system had no philosophical basis, and it quickly fell into disuse. After the discovery of isomorphism, an endeavour was made by Graham to arrange the simple bodies in accordance with their natural relations, and even before 1850 the various elements were grouped by him very much as now.

This scheme of classification, somewhat modified by considerations of valency, and occasionally corrected by more accurate information concerning true analogies (as when vanadium was transferred by Roscoe to the nitrogen group), was in general use for practically a quarter of a century—in fact, until it was superseded by the gradual adoption of Mendeleeff's arrangement based on periodicity. There can, however, be little doubt that this attempt by Graham at a natural classification paved the way along which Newlands and eventually Mendeleeff were led to devise our present rational system of grouping the chemical elements.

The numerical relationships existing among the equivalents and atomic weights of the elements of certain of these groups, pointed out by Dumas, Pettenkofer, Odling, Gladstone, and others, gave rise to much speculation. The values of the gradational differences, of course, depended upon whether equivalents or atomic weights were employed; but the immediate point is that, whichever basis was adopted, definite numerical relations were to be perceived. Thus, in the case of the group of the halogens, it was pointed out that the individual members are connected together as follows :—

Fluorine.	Chlorine.	Bromine.	Iodine.
19	35.5	80	127
$a$	$a+d$	$a+2d+d'$	$2a+2d+2d'$

where  $a=19$ ;  $d=16.5$ ;  $d'=28$ .

Thus, too, in the case of the nitrogen group :—

Nitrogen.	Phosphorus.	Arsenic.	Antimony.	Bismuth.
14	31	75	119	207
a	a+d	a+d+d'	a+d+2d'	a+d+4d'

where a=14; d=17; d'=44.

On the basis of these and similar numerical relationships it was surmised that, just as the successive members of a group of homologous organic radicals are formed by increments of  $\text{CH}_2$ , so the substances in the several groups of the elements may be produced by successive additions of some form of matter common to them all. This has its counterpart, somewhat modified, in the modern hypothesis of the disintegration of the elements. Dumas conceived the elements in any particular group to be built up by successive accretions of particular forms of matter; Rutherford and Soddy suppose them to be derived by the successive elimination of matter from some unstable parent substance.

Since 1850 the existence of at least twenty-two new elements may be said to have been established. Of course, many more than this number have been announced, more or less tentatively; but subsequent investigation has either not confirmed their existence, or has definitely disproved it. The names, symbols, and atomic weights of the twenty-two, arranged in alphabetical order, are as follows :—

Argon	A	39.9	Neodymium	Nd	144.3
Cæsium	Cs	132.8	Neon	Ne	20.0
Dysprosium	Dy	162.5	Praseodymium	Pr	140.6
Europium	Eu	152.0	Radium	Ra	226.4
Gadolinium	Gd	157.3	Rubidium	Rb	85.4
Gallium	Ga	69.9	Samarium	Sa	150.4
Germanium	Ge	72.5	Scandium	Sc	44.1
Helium	He	4.0	Thallium	Tl	204.0

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Indium	In	114.8	Thulium	Tm	168.5
Krypton	Kr	83.0	Xenon	Xe	130.7
Lutecium	Lu	174.0	Ytterbium	Yb	172.0
			(Neoytterbium)		

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The additions have been due, to some extent, to the refinement of processes of analysis already in use, but more especially to the employment of new analytical methods; or, lastly, to the application of a generalisation concerning the mutual relations of the elements which has served to indicate not only the existence of new and specific members of families of elements already known, but to point out the probable mode of their occurrence.<sup>1</sup>

Although the existence of the element *fluorine* was surmised as far back as 1771, when Scheele first recognised that the product of the action of oil of vitriol upon fluor-spar contained a hitherto unknown substance, it was not until 1886 that this substance was definitely isolated by Moissan by the electrolysis of the acid potassium fluoride in solution in hydrogen fluoride. Cerium tetrafluoride,  $\text{CeF}_4$ , and lead tetrafluoride,  $\text{PbF}_4$ , when heated, were observed by Brauner to evolve a gas having a smell resembling that of hypochlorous acid, which was probably free fluorine. Certain violet-coloured varieties of fluor-spar, when powdered, emit a peculiar smell, which has been attributed to free fluorine.

Gore observed that anhydrous hydrogen fluoride would not conduct electricity—a fact confirmed by Moissan. Moissan found, however, that on adding

<sup>1</sup> The substances which appear to be formed by the disintegration of uranium, radium, thorium—the so-called radio-active elements—such as *ionium*, *actinium*, *polonium*, and the various *emanations* to which they give rise, are not here enumerated. They are dealt with in Chapter III.

potassium fluoride to the liquid it readily suffered electrolysis with the liberation of free fluorine as a light greenish yellow gas with a pungent, irritating smell resembling that of hypochlorous acid. It has a vapour density corresponding with an atomic weight 19. By the application of cold and pressure it may be liquefied. At still lower temperatures it may be frozen to a white solid. Fluorine is characterised by an extraordinary chemical activity, and combines, even at ordinary temperatures, with a large number of substances. Sulphur, phosphorus, arsenic, antimony, boron, iodine, and silicon inflame or become incandescent in contact with it. It combines with hydrogen with explosive violence, even in the dark and at the lowest temperature. It unites also with the metals, occasionally with incandescence, and decomposes water with liberation of oxygen.

The application, by Bunsen, of the *spectroscope* to chemical analysis almost immediately resulted in his discovery, in 1860, of *cæsium*, and, in 1861, of *rubidium*. Cæsium was first detected in the mineral water of Dürkheim in the Palatinate and in the mineral petalite, by the two blue lines it forms in the spectrum, whence its name from the Latin *cæsius*, used to designate the blue of the clear sky. Rubidium was found in a lepidolite by means of a number of lines in different parts of the spectrum not previously observed, two being especially remarkable in the outermost region of the visible red portion—whence the name of the element from the Latin *rubidus*, used to designate the darkest red colour. The new metals were found to have the closest analogies to potassium, with which they usually occur associated in nature. Rubidium is found in a number of lepidolites, leucite, spodumene, triphylite, mica, and orthoclase, and in the Stassfurt carnallite; in



sea-water and in many mineral waters. It occurs also in the ashes of many plants, such as those of beetroot, tobacco, tea, coffee, etc. It is doubtful if it is a normal constituent of plant food, attempts to introduce it in place of potash having failed. It is not improbable that these elements would have remained unknown except for spectrum analysis. At all events, one of them—cæsium—was missed in 1846 by Plattner, in the course of the analysis of the mineral *pollucite*, in which it occurs to the extent of one-third of its weight. After the discovery of cæsium by Bunsen, this mineral was again analysed by Pisani, when it was found that the alkali which Plattner had mistaken for potassium was in reality cæsium. Cæsium is found to a very small extent in many mineral waters, in a variety of minerals, and in the ashes of plants.

In 1861 Sir William Crookes made known the existence of a new element which he called *thallium*. He found it in a seleniferous deposit obtained from an oil of vitriol factory in the Harz. It was characterised by giving a bright green line in the spectroscope—whence its name from *θαλλός*, a green or budding twig. The discovery was confirmed in the following year by Lamy. Thallium, in its general chemical relations, has many analogies to the metals of the alkalis, although in the metallic state it has the closest resemblance to lead. It occurs in many varieties of pyrites, in a few minerals, such as crookesite, lorandite, zinc-blende and copper pyrites, etc., and in certain mineral waters.

In 1863 Reich and Richter, by means of the spectroscope, detected the presence of a new element in the zinc-blende of Freiberg. The observation that it afforded two indigo-blue lines in the spark-spectrum led them to give it the name *indium*. It has since been found in

numerous blendes, in various zinc and tungsten ores, and in many iron ores. It is a silver-white ductile and malleable metal, melting at  $174^{\circ}$  and burning when heated with a violet flame. It is related in chemical characters to aluminium and zinc. Its true place in the natural scheme of classification of the elements was indicated by Mendeléeff.

In 1875 Lecoq de Boisbaudran discovered a new element in the zinc-blende of Pierrefitte in the Pyrenees, also by means of spectrum analysis. The spark spectrum of its salts affords two characteristic violet lines quite different in position from those given by indium. To the new element its discoverer gave the name of *gallium*. It has been found in very small amounts in other blendes, but is still one of the rarest of the chemical elements. It is a bluish-white, hard, and slightly malleable metal, fusing at a temperature not much higher than that of a hot summer day. Its existence and main properties, as well as its more significant chemical relationships, were predicted by Mendeléeff in 1869 from considerations based upon his periodic law. (See *ante*.)

In the same year Mendeléeff also predicted the existence of a new element belonging to the group of which boron is the first member, which he provisionally termed *eka-boron*, and described its main properties. Mendeléeff's prediction was verified in 1879 by Nilson's discovery of the element *scandium*. Scandium occurs associated with yttrium, ytterbium, etc., in many Swedish minerals, such as *euxenite*, *gadolinite*, *yttrötitanite*, etc. The metal itself has not been isolated, but the properties of its compounds correspond closely with those of the corresponding ekaboron compounds, as predicted by Mendeléeff.

A further illustration of the value of the principle of periodicity, as developed by Mendeléeff, in indicating the existence of new elements, is seen in the discovery of *germanium*. In 1885 Weisbach discovered a new Freiberg silver mineral, to which he gave the name *argyrodite*. This on analysis by Winkler was found to contain a new element to the extent of about seven per cent. with properties identical with those predicted by Mendeléeff for a missing element in the fourth group of the periodic series, consisting of silicon, tin, and lead, and which he had provisionally termed *eka-silicon*. *Argyrodite*, in fact, is a double sulphide of silver and germanium,  $2\text{Ag}_2\text{S} \cdot \text{GeS}_2$ . Germanium is a greyish-white, lustrous metal of sp.gr. 5.5., melting at about  $900^\circ$ , and resembling silicon and tin in its general chemical relations.

*Dysprosium*, *europium*, *gadolinium*, *lutecium*, *neodymium*, *praseodymium*, *samarium*, *thulium*, and *ytterbium* (*neoytterbium*) belong, like scandium, to the group of the so-called rare-earth metals. These substances have been detected in a great variety of minerals, many of which are extremely rare. The elements most frequently occur in nature associated with yttrium, cerium, thorium, and zirconium.

*Dysprosium* was first detected, in 1886, by Lecoq de Boisbaudran in the so-called erbium earth of Mosander, in which Cleve had previously (1880) announced the existence of two other elements, *holmium* and *thulium*. There is some reason to believe that the holmium of Cleve is identical with dysprosium. *Ytterbium* was discovered by Marignac, in 1878, in the mineral *gadolinite*. In 1906 Auer von Welsbach announced that Marignac's ytterbia was a mixture, which was confirmed

in the following year by Urbain, who separated it into two elements, which he named *neoytterbium* and *lutecium*. *Europium* was discovered by Demarçay in 1901. All these earths are met with in small quantities associated with yttria in *gadolinite*, *euxenite*, *samaraskite*, *xenotime*, *cerite*, *orthite*, and other similar minerals. Their compounds, or such of them as have been described, resemble the corresponding compounds of yttria. They are recognised by differences in their spectroscopic behaviour. *Gadolinium* was detected, independently, in 1886, by Marignac and Lecoq de Boisbaudran in the terbium earth of Mosander.

What was long known as *didymium* (διδυμος=a twin) was discovered by Mosander in 1841. It owes its name to its close chemical relationship to, and almost constant association with, *lanthanum*—both elements occurring in many minerals, more particularly in *cerite*, *allanite*, and *monazite*. In 1885 Auer von Welsbach announced that the didymium of Mosander was, in reality, a mixture of two elements which could be separated by the systematic fractional crystallisation of the double ammonium nitrates; to these elements he gave the names *praseodymium* (πράσινος, a leek-green) and *neodymium* (νέος, new). Neodymium salts are rose-coloured, whereas those of praseodymium are green, and the elements are further characterised by differences in their absorption and spark spectra. When mixed, the substances give the spectrum originally considered to be characteristic of didymium.

*Samarium* was discovered in 1879 by Lecoq de Boisbaudran in *samaraskite*. Its salts are yellow, and afford in solution characteristic absorption bands.

It is not improbable that many of the minerals from which the so-called rare earths are obtained contain

elements hitherto unrecognised, and it is possible that certain of the substances now assumed to be elements may, like didymium, turn out to be mixtures. In fact, additional elements have from time to time been announced, as, for example, the *decipium* of Delafontaine (1878) and the *monium* or *victorium* of Crookes (1899), pronounced by Urbain to be identical with gadolinium: their individuality cannot as yet be said to be established. Didymium itself was stated by Krüss and Nilson (1888) to be even more complicated than the work of Auer von Welsbach would seem to indicate, and to contain no fewer than eight elementary substances. As yet, however, no confirmation of this surmise has been obtained.

The chemistry of the rare earths has of late years been greatly extended owing to the employment of certain of the members of the group in the manufacture of the "mantles" used in gas-lighting, and which consist substantially of thoria, mixed with about one per cent. of ceria. Large quantities of *monazite*, *thorianite*, *thorite*, *cerite*, and other minerals, are now worked up for the sake of the thoria and ceria they contain, and considerable amounts of residual products, consisting largely of other members of the family, are now available for investigation. It is reasonably certain, therefore, that our knowledge of this section of inorganic chemistry will be largely augmented in the immediate future. Indeed, the application of thoria to the construction of gas-mantles may be said to have removed that substance from the category of the rare elements. No sooner was it discovered that it was capable of useful application than unexpected sources of supply were found.

The same result has followed in other cases. One of

the most significant developments of modern chemistry is seen in the efforts which are constantly being made to turn the so-called rare elements to useful account; and when they are found to be technically valuable it is generally observed that hitherto unknown sources of supply are soon available. Cerium salts have been found to be useful in the colouring of glass and porcelain, as mordants in dyeing, in photography, and in medicine. Zirconium has been used in incandescent electric lighting, and thallium has been employed in the manufacture of highly-refractive optical glass. Titanium, molybdenum, and vanadium are used in the manufacture of steel of high tensile strength. Tantalum and tungsten are employed in the construction of filaments in incandescent electric lighting. Tantalum, indeed, has been found to occur in considerable quantities, and to be more largely distributed than was hitherto supposed. Alloys of tungsten and aluminium are used in automobile construction, and alloys of tungsten, aluminium, and copper in the manufacture of propeller blades. Tungsten steel is used in armour plates, and to stiffen the springs of cars; in the manufacture of piano-wire, and to increase the permanency of magnets. Even the rarer metals of the platinum group are finding many important applications. Osmium-iridium is used for the bearings of compasses, for the tips of gold pens, and in the construction of standard weights. Osmium and rhenium enter into the composition of filaments for electric lighting. The extraordinary influence of light on the electric conductivity of selenium has been made use of in the transmission of photographs by telegraph and telephone wires, and for measuring the light intensity of the Röntgen rays in clinical work.

## CHAPTER III.

### THE INACTIVE ELEMENTS : RADIUM AND RADIO-ACTIVITY

*Argon, helium, krypton, neon, and xenon* belong to the group of the so-called inactive elements, and constitute what are known as the rare gases of the atmosphere. The existence of these bodies is of great theoretical value, and few discoveries of recent times have excited more interest and curiosity. Twenty years ago it was generally assumed that practically all that was to be known concerning the composition of atmospheric air had\* been ascertained. Priestley and Cavendish had recognised that it was mainly composed of oxygen and nitrogen, and Cavendish had definitely stated that these gases are present in practically constant proportion, independent of season, climate, or locality. Thénard, Saussure, and others, had determined the limits of variation in the amount of carbon dioxide. Bunsen and Regnault had established that the quantities of oxygen and nitrogen are subject to slight alteration, the extent of which could be readily determined by the exact eudiometric processes they had devised. Lastly, it was proved beyond a doubt that the gases of the atmosphere are simply mechanically mixed, and can be separated by a variety of physical methods. In fact, of no single subject could it be more confidently assumed that finality of knowledge had apparently been reached.

In 1892, in the course of a series of determinations of the densities of the common gases, Lord Rayleigh found that the density of nitrogen obtained from the air was slightly greater than the density of that gas prepared by the decomposition of ammonia and of nitric acid, the difference in weight being about 1 part in 200—an amount far greater than could be accounted for by errors of weighing. Various suppositions were made in explanation of the discrepancy; but these, when tested, were found not to account for the facts. By heating the atmospheric nitrogen with metallic magnesium, whereby the greater portion of the gas is absorbed to form the nitride, Sir William Ramsay found that the density of the residual gas was still further increased, which rendered it probable that the relatively high density of atmospheric nitrogen, as compared with that derived from ammonia, and, as Lord Rayleigh found, from other sources also, was due to the presence of a gaseous substance in the air of considerably greater density than nitrogen or oxygen. Lord Rayleigh also subjected atmospheric nitrogen mixed with oxygen to the electric discharge over a solution of caustic soda, in a manner similar to that already employed by Cavendish, and found also that the residual gas was considerably increased in density. At the Oxford meeting of the British Association in August, 1894, the two investigators were in a position to announce that the discrepancy was actually due to the presence of a hitherto unknown gaseous constituent of atmospheric air, considerably more soluble in water than nitrogen, and to which, on account of its chemical inertness, the name of *argon* (ἀργόν, idle) was given. By a special apparatus devised by Lord Rayleigh, in which a mixture of air and oxygen is submitted to an



electric flame produced by a powerful, rapidly alternating current, considerable quantities of argon were separated from the air. It has also been found that, by the use of metallic calcium or a mixture of magnesium and lime, the atmospheric nitrogen is absorbed at a lower temperature, and more rapidly than by magnesium alone.

Argon has been found to exist in the gases from springs and mineral waters, notably in those of Bath, Cauterets, Wildbad, and Harrogate. It has also been found in a meteorite, in the gas occluded in rock-salt, and in the minerals *malacone*, *uraninite*, *bröggerite*, etc. No animal or vegetable substance appears to contain it. It is present in atmospheric air to the extent of about one per cent. by volume. It is a colourless gas of an atomic weight of 39.9: one litre of it at the standard temperature and pressure weighs 1.7815 grams. Experiments made by the method of Kundt and Warburg—*i.e.*, by determining the ratio of the specific heats at constant pressure and constant volume by the velocity of sound in the gas—prove that argon, like mercury gas, is monatomic. This of itself indicates that argon is an element, since a monatomic compound is a contradiction in terms. The calculations from the experimental data presuppose that argon obeys the laws of Boyle and Dalton, which was found on trial to be the case. By the application of cold and pressure argon can be liquefied. The liquid boils at  $-186^{\circ}.1$  and freezes at  $-187^{\circ}.9$ . The spectrum of the gas is exceedingly complicated, consisting of a great number of lines extending throughout the visible portion and far into the extreme red and ultra-violet. The colour of the light emitted on sparking the gas changes with increase of temperature from a brilliant red to a bright blue—depending on the

intensity, of the discharge. All attempts to induce argon to enter into combination with other substances have failed. The methods of its preparation show that it does not combine with oxygen, although Troost and Ouvrard state that it unites with magnesium vapour. It forms no compounds with hydrogen, chlorine, phosphorus, sulphur, sodium, tellurium, etc. Even fluorine, probably the most generally active of the chemical elements, shows no tendency to unite with it.

In 1888 Dr. Hillebrand, of the U. S. Geological Survey, in examining a form of uraninite known as *cleveite*, so named from the late Professor Cleve, found that on treatment with dilute sulphuric acid it gave off considerable quantities of a gas which was assumed to consist only of nitrogen, as it gave the spectroscopic reactions of that element. To test whether this gas contained argon, Ramsay, in 1895, further examined it spectroscopically. After sparking it with oxygen in the presence of caustic soda solution, in the way already described, it gave no indications of argon. The main characteristic of its spectrum was a bright yellow line, known as  $D_3$ , not coincident with that afforded by sodium, but identical, in position with a line detected in the chromosphere during the solar eclipse of 1868, which line, on examination by Frankland and Lockyer, could not be ascribed to any known element. For this supposed new element the name *helium*, from *ἥλιος*, the sun, had been suggested. This was the first occasion on which an element observed originally only in the sun was found to occur also on the earth. The presence of the new element in the gas from *cleveite* was subsequently confirmed by Langlet working in Cleve's laboratory.

Helium is a monatomic gas having the atomic



SIR WILLIAM RAMSAY.

weight 4. It is less soluble in water than argon. Like argon, it shows no tendency to enter into chemical union with any other substance. It has been found in many minerals, particularly in those containing uranium and the so-called rare earth metals. It also occurs among the gases issuing from certain mineral springs, such as those of Bath, and at Cauterets in the Pyrenees, and also at Adano near Padua. The spectrum of helium contains, in addition to the characteristic yellow line—by which its presence had been recognised not only in the solar chromosphere, but also in certain of the fixed stars—two lines in the red, and lines in the green, blue, and violet. The character of the light emitted by the spark-discharge is modified by the intensity of the discharge in a manner similar to that of argon. It has been shown by Collie that its spectrum is altered by the presence of mercury vapour. It is the least refractive of all the gases. Helium was liquefied by Kammerlingh Onnes in 1908. It forms a colourless liquid of sp. gr. 0.154, boiling at  $-268.5$ —that is,  $4^{\circ}.5$  above the absolute zero of temperature. Its critical temperature is about  $5^{\circ}$  absolute, and its critical pressure above  $2\frac{1}{4}$  atmospheres.

The methods now in use for obtaining liquid air, referred to in a subsequent chapter, enable large quantities of that material to be obtained readily; and it was in investigating spectroscopically the residues left after volatilising a quantity of liquid air that Ramsay and Travers, in 1898, detected the existence of two new monatomic gaseous constituents of the air which they named respectively *krypton* (κρυπτός, hidden) and *neon* (νέος, new), the former heavier and the latter lighter than argon. By fractional distillation of the argon, simultaneously procured, a gas was obtained

which in the spectroscope showed the characteristic lines of helium—previously recognised in atmospheric argon by Kayser and Friedländer—together with a complicated spectrum consisting of a number of lines in the red, orange, and yellow due to the new element neon. On cooling this mixture to  $-252^{\circ}$  by means of liquid hydrogen, the neon solidified, while the helium remained gaseous and could thus be separated.

Krypton was obtained from the residues left on the evaporation of a large quantity of liquid air. Mixed with the krypton was a third gaseous constituent of air, to which the name *xenon* ( $\xi\epsilon\nu\omicron\varsigma$ , the *stranger*) was given. The boiling point of krypton at atmospheric pressure was found to be  $-152^{\circ}$ , and its melting point  $-169^{\circ}$ ; the boiling point of xenon was  $-109^{\circ}$ , and its melting point  $-140^{\circ}$ . Their critical temperatures were respectively  $-62^{\circ}.5$  and  $+14^{\circ}.7$ . Hence xenon could be liquefied by pressure at very little below the mean temperature of the air. Neon boils at  $-243^{\circ}$  and freezes at  $-253^{\circ}$ . They form colourless liquids freezing to ice-like solids. All of them, with the exception of argon, which is present to the extent of about 1 part in 107 parts of air, are contained in extremely small amounts in the atmosphere, approximately in the following proportions:—

Helium	1 part in 245,300	parts by volume.
Neon	1 " " 80,800	" "
Krypton	1.° " " 20 millions,	" "
Xenon	1 " " 170	" " "

Many tons of liquefied air have since been systematically fractionated, but no other gas than those above named has been obtained.

Julius Thomsen, of Copenhagen, in a paper published in 1895, entitled *On the Probability of the Existence*

of a *Group of Inactive Elements*, pointed out, in relation to Mendeléeff's Law of Periodicity (see *ante*), that in periodic functions the change from negative to positive value, or the reverse, can take place only by a passage through zero or through infinity; in the first case the change is gradual, and in the second case it is sudden. The first case corresponds with the gradual change in electrical character with rising atomic weight in the separate series of the periodic system, and the second case corresponds with a passage from one series to the next. It therefore appears that the passage from one series to the next in the periodic system should take place through an element which is electrically indifferent. The valency of such an element would be zero, and therefore in this respect also it would represent a transitional stage in the passage from the univalent electronegative elements of the seventh to the univalent electropositive elements of the first group. This indicates the possible existence of a group of inactive elements with the atomic weights 4, 20, 36, 84, 132—numbers corresponding fairly closely with the atomic weights respectively of helium, neon, argon, krypton, and xenon.

No discovery of recent years has created more widespread interest than that of the radio-active elements.

In 1896 Henri Becquerel found that uranium salts emitted an invisible radiation which had the power of affecting a photographic plate, even though not directly exposed to it, exactly in the same way as the Röntgen or X-rays. Since that time a number of substances have been shown to possess a similar property. Such substances are said to be radio-active. The radiation emitted by them is not uniform in character. It

has been found to be of three distinct types, known respectively as the  $\alpha$ ,  $\beta$ , and  $\gamma$  radiations. The  $\alpha$  rays consist of positively electrified particles moving with a velocity equal to about a fifteenth of that of light. These rays have little penetrative power, and are capable of being deflected by a magnet.

The  $\beta$  rays consist of negatively electrified particles of a mass not greater than one-thousandth of that of the hydrogen atom, and they move with a velocity approximating to that of light. The  $\beta$  rays have a greater penetrative power than the  $\alpha$  rays, and are even more readily deflected by a magnet.

The  $\gamma$  rays are analogous to, if not identical with, the X or Röntgen rays; they move with the velocity of light, have a high penetrative power, but are not affected by the magnet. All three forms of radiation render gases electrically conductive, excite luminescence or fluorescence in certain substances, change the colour of glass, convert oxygen into ozone and yellow phosphorus into red phosphorus, and act upon photographic plates.

According to the disintegration theory of Rutherford and Soddy, the radio-active elements are forms of matter undergoing changes resulting in the formation of new forms possessing chemical and physical properties differing from those of the parent substance, these changes being accompanied by the production of sensible heat, or some other manifestation of energy, due to the process of transformation of the changing atoms. The rate of change is found to be different for each radio-active element, but to be constant for the same element irrespective of its particular form of combination. The relative radio-activity of the various chemical combinations of a given radio-active

element is directly proportional to the quantity of the element contained in them. The process of disintegration may be carried through a number of intermediate products until a stable form is produced. Uranium, in which the phenomenon of radio-activity was first perceived, is supposed to give rise to no fewer than seventeen different forms of matter, including *radium*, *actinium*, and *polonium*. Thorium, another radio-active element, is supposed to disintegrate into eight different forms of matter. Uranium disintegrates with extreme slowness; it is calculated that in a year not more than one ten-billionth part of the uranium is transformed. The first disintegration product is termed uranium X. If a quantity of dehydrated uranium nitrate be treated with ordinary ether, a slight residue is obtained which is found to contain uranium X. It emits  $\beta$  and  $\gamma$  rays, and is relatively rapidly transformed into other substances. Ordinary uranium, freed from uranium X, only emits  $\alpha$  rays. Uranium salts can be freed from uranium X by repeated crystallisation, uranium X remaining in the mother liquors.

The existence of radium was first made known by **Mme. Curie** in 1898. In examining certain uranium minerals and uranium products, Mme. Curie observed that their radio-activity was apparently greater than that corresponding with the amount of uranium contained in them, and she was led to surmise that this might be due to the presence of some constituent more strongly radio-active than uranium. This supposition proved to be well founded, and she eventually succeeded in isolating a new element termed *radium*, forming compounds with characters and relationships akin to those of barium. The richest source of radium at present known consists of certain residues occurring





MARIE CURIE (*née* SKŁODOWSKA).

at Joachimsthal, in Bohemia, left after the extraction of uranium from pitch-blende, in which radium occurs to the extent of 0.2 gram per ton. These residues are mainly sulphates of lead and calcium, mixed with a great variety of other metallic compounds. To obtain the radium the mixture is heated with concentrated caustic soda solution, the residue washed with water and treated with hydrochloric acid which dissolves the greater portion of the material. Nearly the whole of the radium is left in the insoluble portion. This, after washing with water, is boiled with a solution of sodium carbonate so as to transform the alkali-earths into carbonates. These are converted into chlorides or bromides, from which, by repeated crystallisation, barium chloride or bromide is obtained, containing the greater portion of the radium as a halide salt. The radium and barium salts are then separated by fractional crystallisation, the radium salts being slightly less soluble in water and alcohol, and in solutions containing the halogen acid, than the barium salt.

Pure radium chloride ( $\text{RaCl}_2$ ) is a white crystalline salt, resembling barium chloride, with which it appears to be isomorphous. Radium, like barium, forms an insoluble carbonate and sulphate, but a soluble nitrate and bromide. The bromide is much less stable than the chloride; on standing it evolves bromine and becomes basic. Radium has as yet been obtained in such small quantities that very few of its compounds have been prepared.

The rays from radium salts burn the skin, and are found to be useful in the destruction of rodent ulcers; they appear to act upon proteids, destroy bacteria, bleach chlorophyll, and affect the germinative power of seeds. A pure and freshly-prepared salt of radium

seems to emit only  $\alpha$  rays, but it soon forms disintegration products, and then gives out, in addition, the  $\beta$  and  $\gamma$  rays.

In the process of disintegration the salts emit heat corresponding to about 75 gram calories per hour for each gram of radium present; their temperature is thus uniformly higher than that of their environment. One product of the change, probably connected with the emission of the  $\alpha$  rays, is the gas helium.

Radium has an atomic weight of 226.5. It is regarded as a product of the disintegration of uranium, the atomic weight of which is 238.5. It is believed to have been formed through an intermediate product known as *ionium*, a radio-active element discovered by Boltwood in the mineral *carnotite*. The atomic weight of ionium is surmised to be about 230. Radium itself is supposed to form at least eight disintegration products, the first of which is the so-called *emanation*, discovered by Dorn in 1900, an inactive gas with an atomic weight of about 180, giving a bright line spectrum, decomposing into helium, liberating oxygen and hydrogen from water, and capable of being condensed to a liquid and solidified at a low temperature. Ramsay and Gray have determined its physical constants. The liquid is phosphorescent, and shines with a colour depending on the nature of the glass of the vessel which contains it. The solid is also phosphorescent, the colour varying with the temperature. It gives out only  $\alpha$  rays, and in its disintegration, like radium, evolves heat. Its position in the Periodic Table is probably above that of xenon. Other products are known as *radio-lead* and *polonium*. The latter substance was identified by M. and Mme. Curie in 1898, and was the first of the strongly radio-active substances to be recognised. In

the periodic system it seems to follow bismuth and to be a member of Group VI., with a possible atomic weight of 210. Its spectroscopic characters have recently been examined by Mme. Curie and Debierne, who have shown that in its decay it evolves helium.

The rate of disintegration of radium is relatively slow; it has been calculated that the time required for half of any given quantity of radium to change completely into other products is about 2,000 years. Rutherford has calculated that in 26,000 years a kilogram of radium would be reduced to one milligram of active substance, the remainder having passed into degradation products.

In 1899 Debierne announced the existence of another radio-active element contained in uranium minerals, which he termed *actinium*. This is probably a disintegration product of uranium and identical with the *emanium* of Giesel. It occurs associated with the rare earths which can be separated from the pitch-blende residues, and is eventually found in the lanthanum salts. Nothing is known as to its atomic weight or its chemical relationships. It undergoes change, and forms, apparently, a gaseous emanation which rapidly disintegrates and can be condensed to a liquid at a low temperature. Four other successive products have been identified by the character of the radiation they emit, their degradation constants, and the time required for one-half of any given quantity to disintegrate into other forms of matter.

*Thorium* was shown to contain a radio-active element by Mme. Curie and Schmidt, independently, in 1898. Whether thorium is itself active is doubtful. The rate of disintegration of *radio-thorium* is probably greater than that of uranium. It, too, seems to form a gaseous

emanation, which can be condensed at the temperature of liquid air and appears to be an inert gas of high molecular weight with the characteristics of the argon family.

The type of radiation emitted by the several products has been observed, and their constants of change and half-value periods calculated ; but little or nothing is known at present concerning their atomic weights, spectroscopic or chemical characters.

## CHAPTER IV.

### ATOMS AND MOLECULES : ATOMIC WEIGHTS AND EQUIVALENTS

It has already been pointed out that the discovery by Gay Lussac, and independently by Dalton, that gases combine in simple proportions by volume, and that the volume of the gaseous product, measured under comparable conditions of temperature and pressure, stands in simple relation to the volumes of the constituents, seemed to most of Dalton's contemporaries, but not to Dalton himself, to afford strong evidence of the validity of his explanation of the essential nature of chemical combination. It appeared obvious from the facts that there must exist some simple relation between the densities, or specific gravities, of the elementary gases and their atomic weights. When, however, the principle underlying Gay Lussac's law was extended so as to include gases in general—both simple and compound—difficulties were met with which were only satisfactorily cleared away during the latter half of the nineteenth century. The first rational attempt to explain the facts observed by Dalton and Gay Lussac, concerning the volumetric relations of gases, was made in 1813 by Amedeo Avogadro by the assumption that a given volume of all gases—simple or compound—contains the same number of integral molecules; hence the relative weights of these volumes represent the relative weights of the molecules. According to Avogadro, in the case of the simple gases the integral

molecules are composed of a certain number of elementary molecules of *the same kind*, whereas the integral molecules of compound gases and vapours are made up of elementary molecules of *different kinds*. The *elementary molecule* of Avogadro is now termed the *atom*; his *integral molecule* we call simply a *molecule*. Similar conceptions were published independently by Ampère in 1814. It follows from the doctrine of Avogadro and Ampère that, as the number of integral molecules is the same in equal volumes of all gases, these molecules must be equidistant from each other, their mutual distances depending upon pressure and temperature. This at once serves to explain the laws of Boyle and Dalton that gases, no matter what their chemical nature, behave identically, as regards change of volume, when compressed by pressure or expanded by heat.

The true significance of the hypotheses of Avogadro and Ampère was long obscured, first on account of their imperfect appreciation by the great leaders of chemical thought during the first half of the nineteenth century—Berzelius, Gay Lussac, Wollaston, and Gmelin—and, secondly, on account of the almost universal practice of deducing atomic weights from purely chemical considerations of equivalence. At the same time, it must be admitted that the recognition of the value of these hypotheses was still further retarded by the seeming anomalies which resulted from a more extended knowledge of the vapour densities of elements and compounds. Thus the vapour densities of mercury, sulphur, phosphorus, and arsenic, as ascertained by Dumas and Mitscherlich, were plainly inconsistent with chemical analogies and the law of Dulong and Petit. So, too, what appeared to be

the vapour densities of sal-ammoniac, phosphorus pentachloride, sulphuric acid, calomel, and of other substances that might be mentioned, were not in accordance with the values demanded by other well-ascertained facts.

By the middle of the nineteenth century the hypothesis of Avogadro was practically forgotten and the law of volumes ignored. The atomic weights of the elements, and the system of notation universally employed in England and Germany, were based wholly upon equivalents. The anomalies thus created were clearly pointed out by Gerhardt, and subsequently by Laurent, who showed how a consistent and harmonious explanation of the facts could be reached by regarding as true equivalents equal volumes—for example, of steam, ammonia, hydrogen chloride, carbon dioxide, marsh gas, etc.; by assuming, in other words, that equal numbers of the molecules of these various substances are contained in equal volumes of the gases, as contended by Avogadro and Ampère. The simplicity and consistency of the new notation gradually won for it the adhesion of chemists. This adhesion was facilitated by the memorable researches of Williamson on etherification, of Gerhardt on the anhydrides, and by the work of Frankland on the radicals; and it reached its logical conclusion when **Cannizzaro**—on the basis of Avogadro's hypothesis—discussed, in 1858, the true atomic weights of the metallic elements as distinguished from their equivalent values. In certain of its aspects the new table of atomic weights drawn up by Cannizzaro resembled that originally proposed by Berzelius; but the numbers adopted by the Swedish chemist were founded on no uniform or rational basis, and were frequently inconsistent.





STANISLAW CANNIZZARO.

Our present tables of atomic weight bring, therefore, the values for the several elements into harmony with the doctrine of Avogadro and Ampère, with the law of Dulong and Petit, and with the facts of isomorphism. The values are, in fact, in unison with all the criteria which serve to indicate the atomic weights of the elements. As a result, our present system of notation, which is, of course, based upon these atomic weights, assigns formulæ to compounds which indicate their true relative molecular weights and simplify the accurate expression of their relationships and chemical transformations. One by one the instances of anomalous vapour density, which were so many stumbling blocks to the universal acceptance of a system based upon the law of gaseous volumes, have been shown to be not only not inconsistent with it, but actually so many corroborative proofs. Thus, in the case of ammonium chloride, the observed vapour density of which was found to be practically half its calculated value, it has been proved that the vapour of this salt, when heated to the temperature at which the observations were made, is mainly resolved into molecules of ammonia and hydrogen chloride, which together occupy double the space of the ammonium chloride molecule. Phosphorus pentachloride vapour, on being sufficiently heated, is similarly more or less resolved into phosphorus trichloride and chlorine.

Moreover, it has been found, by a more accurate study of the action of heat upon the vapour of ammonium chloride and of phosphorus pentachloride, that within certain narrow limits of temperature these substances can actually exist as such in the gaseous state, and that the density of their vapours does actually conform to that demanded by theory. Moreover, phosphorus

pentafluoride, the analogue of the pentachloride, is gaseous at ordinary temperatures, and has a normal density. It may be heated to a high temperature without showing any sign of decomposition.

Limitations of space will not allow of a fuller explanation of the apparent anomalies already alluded to. They have each in turn been experimentally attacked and satisfactorily explained. No valid exception is now known to the universal applicability of the principle.

To-day the chemical history of a substance, whether elementary or compound, if vaporisable, is not complete until its vapour density is known, since a knowledge of this constant affords the most certain means of establishing the relative weight of its molecule. Accordingly many chemists have endeavoured to simplify and render more convenient the modes of determining vapour densities. Thanks to the efforts of Hofmann and Victor Meyer, the processes associated with the names of Dumas, Gay Lussac, Deville, and Troost, which have furnished us with valuable information in the past, have now given way to comparatively simple and rapid methods, which, although not necessarily more accurate, furnish the required information with less expenditure of time and trouble; that is to say, they serve to indicate, which of two, or more, presumed molecular weights is correct, and so enable us to establish the molecular formula of the substance. The chemical formula of a substance is a condensed expression of a number of facts connected with its history. Thus the expression  $\text{H}_2\text{O}$ —the chemical formula for water—indicates that the substance is composed of hydrogen and oxygen, in the proportion, using round numbers, of 2 parts by weight of hydrogen and 16 parts by weight

of oxygen ; or, in other words, of 2 atoms of hydrogen, each weighing 1, and 1 atom of oxygen weighing 16. The formula, moreover, connotes the fact that when the gases combine 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of water-vapour (steam). So, too, the formula  $\text{HCl}$ —which represents hydrogen chloride—means that the substance is a compound of 1 atom of hydrogen weighing 1 united with 1 atom of chlorine weighing 35.5 ; it also denotes the fact that in the act of union 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride. Lastly, the formula  $\text{NH}_3$  signifies that the molecule of ammonia is composed of 1 atom of nitrogen weighing 14 and 3 atoms of hydrogen, each weighing 1 ; it further indicates that when ammonia gas is resolved into its constituents, as it can be when sufficiently heated, 2 volumes of ammonia gas are increased to 4 volumes of a mixture made up of 1 volume of nitrogen and 3 volumes of hydrogen.

In short, all the formulæ are what are called *two-volume formulæ* ; that is, the relative molecular weights of the substances occupy the same volume as two relative parts by weight of hydrogen. Hence their vapour densities—referred to hydrogen as unity—are the halves respectively of their molecular weights. Steam is 9 times, hydrogen chloride 18.25 times, and ammonia 8.5 times heavier than hydrogen, when measured under identical conditions of temperature and pressure. The quantities expressed by the formulæ  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{NH}_3$ , occupy the same volume. This is equally true of the quantities expressed by  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{Cl}_2$ , etc. These expressions signify that the molecules of the elements of hydrogen, oxygen, nitrogen, and chlorine consist each of 2 atoms of the respective substances: the molecule

of water consists of 3 atoms—2 of hydrogen and 1 of oxygen; the molecule of hydrogen chloride of 2 atoms—1 of hydrogen and 1 of chlorine; whereas the molecule of ammonia contains 4 atoms—1 atom of nitrogen and 3 atoms of hydrogen.

Certain of the elementary bodies are, as already stated, capable of existing in different allotropic states. Thus there is a modification of oxygen known as *ozone*. This substance has long been recognised as being formed from air under the influence of the electric discharge. It was the subject of study by Schönbein as far back as 1839; but that it was a condensed form of oxygen, and not a peroxide of hydrogen—as was at one time surmised—was first established by Andrews and Tait. The degree of its condensation was definitely ascertained by Soret by observing its rate of diffusion, from which, on the basis of Graham's law, its density could be inferred. It was found to be  $1\frac{1}{2}$  times that of ordinary oxygen. Hence, if the molecule of oxygen consists of 2 atoms, that of ozone consists of 3 atoms. The chemical symbol of ozone is, therefore,  $O_3$ .

It has been found also that the molecule of sulphur, in the state of solution, contains eight atoms. This complex molecule in the gaseous state gradually breaks down as the temperature is increased, and at temperatures above  $850^\circ$  contains, like its analogue oxygen, only two atoms. The molecules of phosphorus and arsenic, in the gaseous state, are each found to consist of four atoms. On the other hand, the molecules of mercury, zinc, and cadmium each consist of only one atom. As will be shown later, Kundt and Warburg established, in 1875, the fact that mercury vapour is a monatomic gas, by determining the rate at which sound is propagated through it. In the same way

it was shown that helium, argon, and its congeners are also, as already stated, monatomic gases.

The applicability of the law of Dulong and Petit to the determination of atomic weights has been frequently exemplified during the last sixty years; and a number of these constants have been rectified by its means—*e.g.*, of thallium, uranium, glucinum, indium, etc. The anomalies presented by the cases of elements of low atomic weight—*e.g.*, carbon, boron, silicon—have been further inquired into; and it has been shown by Weber, and independently by Dewar, that in the case of these substances the specific heat rapidly increases with the temperature, and approximates at high temperatures to a value required by the law of Dulong and Petit.

Within recent years other methods of ascertaining molecular weights have been put at the disposal of chemists. These methods are especially valuable in the case of bodies which cannot be volatilised. They depend upon the influence of the substance (1) upon the freezing-point and (2) upon the boiling-point of a solvent. It has long been known that a substance in solution affects the freezing-point of the solvent, and in the great majority of cases depresses it. Sir Charles Blagden, as far back as 1788, showed that in aqueous solutions of inorganic salts the depression was proportional to the amount dissolved. It was subsequently found by Coppet that, in a number of solutions of similar salts where these were present in the ratio of their molecular weights, the solutions froze at practically the same temperature: the molecular depressions of the freezing-points differ from group to group, but are nearly equal in groups of similar compounds. Raoult further observed that, when certain quantities of the same substance are successively

dissolved in a solvent on which it exerts no chemical action, there is a progressive lowering of the point of solidification of the solution, and this depression is proportional to the weight of the substance dissolved in a constant weight of the solvent. In the case of a large number of solvents the depressions of the freezing-point, calculated for amounts proportional to the molecular weights of the dissolved substance, were nearly constant. Raoult pointed out that these relations between the molecular weights and the lowering in the freezing-point may be employed to determine the molecular weight of a soluble substance. The molecular weight  $m$  is found from the expression  $m = K/A$ , where  $A$  is the quotient obtained by dividing the observed depression in the freezing-point of the solvent by the percentage content of the solution, and  $K$  (the molecular depression) is a constant dependent on the solvent. Thus, in the case of phosphorous oxide it was found that 0.6760 gram added to 20.698 grams of benzene—in which the oxide is soluble without change—lowered the freezing-point of the 3.16 per cent. benzene solution by  $0.68^\circ$ . Since the value of  $K$  for benzene is 49, we have 
$$\frac{3.16 \times 49}{0.68} = 227,$$
 which serves to indicate that  $P_4O_6$  is the true molecular formula for phosphorous oxide. This result is confirmed by vapour density observations.

The effect of adding a substance to a solvent is to diminish the vapour-pressure of the liquid. Hence, since the boiling-point of a liquid is that temperature at which the vapour pressure is equal to the atmospheric pressure, the effect of adding the soluble substance is to raise the boiling-point, since a higher temperature is required in order that the pressure of the vapour shall equal that of the atmosphere. It has

been proved that equal volumes of solutions in the same solvent which have the same boiling-point contain an equal number of molecules of the dissolved substance.

The equation for the molecular increment of the boiling-point for a solvent is  $d = 0.02 T^2/w$ , in which  $d$  is the increment of the boiling-point caused by the solution of one gram-molecule of a substance in 100 grams of the solvent,  $T$  the *absolute* boiling-point of the solvent, and  $w$  the heat of vapourisation of the solvent for one gram. The molecular rise of the boiling-point is therefore independent of the nature of the dissolved substance.

The molecular weight of the substance  $m$  is obtained from the formula  $m = pd/\Delta$ , in which  $p$  = the percentage weight of the dissolved substance,  $d$  = the molecular increment in boiling point ( $0.02T^2/w$ ),  $\Delta$  = the observed rise in boiling point. If the latent heat of vapourisation of the liquid is unknown, the value of  $d$  may be obtained by preliminary experiments with a substance of known molecular weight; in this case  $d = m\Delta/p$ .

The calculation of the molecular weight  $m$  may also be made by the formula  $m = K \frac{s}{\Delta L} \times 100$ , in which  $\Delta$  is the rise in boiling point,  $s$  the weight of dissolved substance,  $L$  the weight of solvent, and  $K$  the molecular boiling point increment. Convenient forms of apparatus for using these methods have been devised by Beckmann, and are now in general use.

From the time of Berzelius, each successive generation of chemists has striven to better the example of that master of determinative chemistry in the effort to obtain accurate values for the atomic weights of the elements.



Among the immediate successors of Berzelius in this work should be mentioned Turner, Penny, Dumas, and Marignac. Dumas in 1859 published the results of an extensive revision of the atomic weights of the elements. On this he based the far-reaching generalisation that, in the language of Prout, "the combining or atomic weights of bodies bear certain simple relations to one another, frequently by multiple, and consequently that many of them must necessarily be multiples of some one unit." Dumas further agreed with Prout that "there seems to be no reason why bodies still lower in the scale than hydrogen (similarly, however, related to one another, as well as to those above hydrogen) may not exist, of which other bodies may be multiples, without being actually multiples of the intermediate hydrogen."

The Belgian chemist, Stas, who had been associated with Dumas in a classical determination of the atomic weight of carbon, set himself to determine, with the highest degree of precision then possible, the atomic weights of about a dozen of the elements, with a view of ascertaining (1) whether an atomic weight is a definite and constant quantity, or whether, as suggested by Marignac, and subsequently by Crookes, an atomic weight represents "a mean value around which the actual weights of the atoms vary within certain narrow limits"; (2) whether, if the atomic weights of the elements are respectively definite and invariable, the numbers are commensurable as alleged by Prout and Dumas; and (3) if it should turn out that the numbers are severally fixed and commensurable, whether this necessarily indicates that the elements are built up of a primordial matter, the *πρώτη ἰλη* of the ancients, referred to by Prout in 1816.

Stas, devoted many years to the solution of these questions, working on a scale and with an accuracy and manipulative skill previously unapproached. The main results of his labour appeared in 1865. He concluded (1) that the atomic weights of the elements are absolutely constant values, and are not affected by the nature of the compounds in which they occur, or the physical conditions of their existence; (2) that the numbers so obtained are not commensurable: to quote his own words: "*On doit considérer la loi de Prout comme une pure illusion.*" Hence the elements must, on the basis of Stas's experimental evidence, be regarded as "*individualités à part*," as he expressed it—each a primordial and unalterable substance.

The appearance of this monumental work, which will ever remain one of the classics of chemistry, created a great impression. Its effect persists to this day. It constituted a model and furnished a standard which each successive worker has striven to emulate, with the result that atomic weights to-day are among the best ascertained of physical constants.

Space will not permit of any detailed account of the work done in connection with atomic weights during the forty-five years which have elapsed since the publication of Stas's memoirs; and the reader who desires fuller information must be referred to the special treatises on the subject, such as the *Constants of Nature* of F. W. Clarke, or the monographs of Meyer and Seubert, Becker, Sebelien, and Van der Plaats.

Reference, however, must be made to the determinations by Lord Rayleigh, Leduc, Morley, Noyes, Guye, Dixon, and Edgar of values which, like those of oxygen, hydrogen, nitrogen, silver, and the halogens,

are largely made use of as fiduciary values in atomic-weight work.

Lastly, it should be mentioned, the re-determination of the atomic weights of the elements with the highest attainable precision and by the most refined and most modern methods has for some years past been a special feature of the work of the Harvard Laboratory, under the direction of Theodore Richards; and some of the most trustworthy and best established values we possess have been ascertained by him and his pupils. Atomic weights are of such fundamental importance that the various nations interested in the pursuit of chemistry have consented to the establishment of an International Committee, which will take cognisance of the work done from time to time in this department of operative chemistry, examine and assess its value, and draw up an annual report on the subject.

Despite the accumulated testimony of this work in relation to the validity of the law of the conservation of mass, the sufficiency of the evidence has now and again been impugned. This aspect of the matter has within recent years been directly investigated by Landolt; and as the result of a painstaking series of experiments, in which every recognised source of error was removed or allowed for, it would appear that there is absolutely no ground for the belief that there is any dissipation of mass in the course of, or as the result of, a chemical change.

## CHAPTER V.

### THE MOLECULAR THEORY OF GASES

THE more obvious physical phenomena of gases were, of course, well known by the middle of the nineteenth century; and the so-called gaseous laws—the laws of Boyle, Dalton, and Gay Lussac—were universally accepted by chemists and physicists at that time as fundamental. That the first two laws were only approximations to truth in a mathematical sense was also well known; and the experimental labours of Regnault and Magnus had not only established limits within which they were inexact, but had, to some extent, indicated the cause of their departure from the ideal condition. The hypothesis of Avogadro, as already stated, was practically ignored at this period, or at least its value was unappreciated until the time of Gerhardt and Laurent, and more particularly Cannizzaro, who in 1858 pointed out its real meaning and made it the keystone in the edifice of modern chemistry.

One of the most significant achievements of the last half-century has been the demonstration that these gaseous laws are interdependent. Their further study, and in particular the study of their variation from exact mathematical expression, has led to a conception of the real nature of a gas which not only comprehends and knits together these laws, but affords a rational explanation of them. If the laws of Boyle and Dalton concerning the relations between pressure, temperature,

and gaseous volume are, and must be from the very nature of the case, only approximations, it follows that the same is equally true of the laws of Gay Lussac and Avogadro, since these are dependent on the others. The definite experimental proof that gases do not actually combine in the precise ratios demanded by the law of Gay Lussac has been forthcoming only during the last twenty years. It has been found that, instead of oxygen and hydrogen combining in the exact ratio of one volume of oxygen to two volumes of hydrogen to form water, as stated by Gay Lussac, one volume of oxygen combines with, according to Scott, 2.00245 vols.; according to Leduc, 2.0024 vols.; according to Morley, 2.00268 vols. of hydrogen. What is true of the volume-ratios in which oxygen and hydrogen are actually found to combine, under ordinary conditions, is no doubt equally true of analogous instances, such as the union of hydrogen and chlorine to form hydrogen chloride. It follows also that the extent of the variation from the mathematical expression of Gay Lussac's law must get smaller and smaller as the combining gases approach the condition of the ideal gas—as they do, for example, under very low pressures. The precise degree of departure from Gay Lussac's law is therefore in a sense accidental, and is dependent upon the conditions under which combination takes place.

The more exact study of the physical phenomena of gases, and in particular the clearer recognition of the causes which determine the extent of their departure from the ideal gaseous laws, have afforded valuable assistance in ascertaining the atomic weights of certain elements independently of chemical considerations. The processes of physical measurement have been so

refined, within recent years that physical methods of arriving at molecular—and, inferentially, at atomic—weights, in the case of all elements and compounds which can be brought into a condition approaching that of the ideal gas, are to be preferred to the gravimetric methods of analysis or synthesis as affording the most probable values of the true atomic weights of the elements. The work of Lord Rayleigh, Leduc, and of Guye and his pupils on the densities of the gases has furnished us with a series of values for the atomic weights of a number of the elements which, in point of accuracy, are as superior to the values of Stas as the values of Stas were superior to those of his predecessors. Daniel Berthelot pointed out in 1898 that the true molecular weight of a gas can be deduced from its density and its observed variations from Boyle's law under atmospheric pressure and at very low pressures. Incidentally, the study of gaseous phenomena has served to place the theory of atoms upon a far more stable foundation than it occupied half a century ago. How halting was the adhesion which even some of the most eminent chemists then gave to this theory was well exemplified by the remarkable lecture given before the Chemical Society of London in 1869, in which Williamson—one of the most sturdy champions of Dalton's doctrine—set forth its true value.

That a gas may be looked upon as an association of particles—hard elastic spheres—moving backwards and forwards in right lines with great velocity, and possessing in the aggregate a very small proportion of the space through which they travel, was first conceived by Daniel Bernoulli in 1738. By means of this hypothesis he explained the direct proportionality between the density and pressure of a gas. If the gas consists of

moving particles, and the pressure which it exerts on the sides of the containing vessel is due to the impacts of these particles, it is obvious that by halving the original volume of the containing space we halve the space through which the particles travel, and therefore double the number of their impacts in a given time ; in other words, by compressing the gas to half its initial volume we double the pressure it exerts, which is nothing else than the law of Boyle. This conception of the nature of a gas is known as the *kinetic theory of gases* ; it was further developed by Waterston in 1845, still more fully by Clausius in 1857, and was subsequently placed in its present position by Maxwell and Boltzmann.

That gases actually do move, and at rates depending on their specific nature, was rendered probable—apart from this explanation of Boyle's law—by many phenomena observed by chemists and physicists in the eighteenth and early part of the nineteenth century. It was known from the observations of Leslie in 1804 that specifically light gases moved or diffused faster than heavy gases. Attempts to determine these rates were made by Schmidt in 1820, and by Graham in 1846, both of whom found that the rate of movement of a gas was independent of its chemical nature, and was determined solely by its mass: *gases move at rates inversely proportional to the square roots of their densities*. The following table given by Graham shows the experimentally ascertained relative rates for a number of gases compared with the rates demanded by the "*law of gaseous diffusion*." Column one gives the name of the gas ; column two, the observed rate of diffusion ; and column three, the square root of the density of the gas (air=1) :—

<i>Gas.</i>	<i>Time of diffusion.</i>	$\sqrt{d}$ <i>density.</i>
Air	1	1
Hydrogen	0.276	0.263
Marsh gas	0.753	0.745
Ethylene	0.987	0.985
Nitrogen	0.986	0.986
Oxygen	1.053	1.051
Carbon dioxide	1.203	1.237

Nitrogen and ethylene are, chemically, totally dissimilar gases, but they have the same density and hence the same rate of movement. As Graham showed, it is possible to separate more or less completely a mixture of gases, if the constituents are of different densities, by taking advantage of their different rates of movement. Such an *atmolytic* method was employed by Rayleigh and Ramsay to prove that atmospheric nitrogen contained argon.

The fact that all gaseous substances, however different their chemical nature, conform in the main to certain simple "laws" indicates the probability that their mechanical structure is similar and comparatively simple. The so-called gaseous "laws"—the laws of Boyle, Dalton, Gay Lussac, Avogadro, and Graham—are to-day, explained on the assumption that a gas consists of an aggregation of molecules, moving incessantly in straight lines and with great rapidity. The rate of movement of the particles is variable by reason of their mutual encounters; at the same instant some are moving rapidly, others more slowly. As already explained, to this ceaseless movement of the molecules is to be ascribed the pressure they exert; the pressure which a gas exerts on any containing surface is the aggregate effect of the impact of its molecules. The law of Boyle states that the product of the volume  $V$  and pressure  $P$  of a given mass of gas



is invariable so long as the temperature is unchanged:  $PV = \text{constant}$ . It was found by Regnault, Magnus, Natterer, and Amagat that all gases, with the exception of hydrogen, show a departure from Boyle's law in the sense that  $PV$  is less than theory demands. In the case of hydrogen  $PV$  is greater than theory. This exception, however, is only apparent. Every gas, if maintained above a certain temperature, shows, after a certain pressure has been reached, a deviation in the same sense as that exhibited by hydrogen.

The deviations from Boyle's law are probably due to two causes: (1) to the effect of cohesion among the molecules, whereby the volume, and hence  $PV$ , is less than theory requires; (2) the molecules are not mathematical points—they have a certain volume; hence, with increasing pressure,  $PV$  is greater than theory demands. The effect of the molecule having a certain magnitude will be clear from the following figure: Let  $M$  be a molecule moving backwards and forwards within a certain space,  $a\ b$ :—



Assume, now, we halve the containing space:—



It will be seen that  $M$ , since its volume is unchanged, will have less than half the original distance to travel or, in other words, it will strike the boundaries of the containing space *more* than twice as frequently in the same interval of time as before; hence  $P$ , and therefore  $PV$ , becomes greater than Boyle's law demands.

It will be noticed, then, that the two causes tending to bring about deviations from Boyle's law act in contrary directions. In the greater number of gases the effect due to cohesion at ordinary pressure is greater than the effect due to the actual space occupied by the molecules. In the case of hydrogen at ordinary temperature the contrary is the case; if, however, hydrogen is strongly cooled, it shows variations similar to those exhibited by other gases at ordinary temperatures. By heating these gases the effect due to cohesion—to the mutual attraction of the molecules—becomes less and less; in such circumstances these gases show departures from theory in the same sense that hydrogen does at ordinary temperatures.

The effect of mutual attraction among the molecules is to make the volume of the gas less than the theoretical value; the cohesive force may therefore be regarded as equal in effect to a certain additional pressure; that is,  $(P + A)V = \text{constant}$ , in which  $A$  is the measure of the force of cohesion.  $A$ , of course, must have relation to the number of molecules mutually attracted:  *$A$  is proportional to the square of the number of the molecules.* But the number of the molecules in the unit volume is proportional to the density of the gas, and in a given mass of gas the density is inversely proportional to the volume. Hence  $A$  is inversely proportional to the square of the volume— $A = a/V^2$ , hence  $(P + a/V^2)V = \text{constant}$ . Now let us trace the effect of the second cause of variation from the mathematical exactitude of Boyle's law. The fact that the molecules are not mathematical points means that  $V$  in the foregoing expression is not identical with the space in which the molecules move. That space is  $V - b$ , in which  $b$  is the measure of the aggregate volume of the molecules.

Hence the true expression becomes  $(P + a/V_1)(V - b) = \text{constant}$ .

The law of Dalton (Charles) also receives its simplest explanation by the kinetic theory of gases; and, moreover, the departures from the mathematical truth of the statement follow as a necessary consequence of the facts that the molecules have sensible magnitudes and are mutually attracted. We can measure the effect of heat upon a gas in two ways. We can either keep the pressure of the gas constant, and measure the increase in volume; or we can prevent the gas from expanding, and measure the elastic force or pressure it exerts. If the law of Dalton were mathematically true, it would follow that, *if the volume of the gas were maintained constant during the heating, its pressure would increase in the same proportion as the volume would have increased if the gas had been allowed to expand, but maintained at a constant pressure*. In other words, the expansion-coefficient and the pressure-coefficient should be the same. Experiment shows, however, that they are not identical.

The following table gives the results of a number of measurements by Regnault :—

	<i>Expansion</i> (Pressure Constant).	<i>Pressure</i> (Volume Constant).
Hydrogen	.003661	.003667
Air	.003670	.003665
Carbon dioxide	.003710	.003688
Sulphur dioxide	.003903	.003845

Variations in the same sense have since been observed by Jolly and Chappuis. With the exception of hydrogen, and probably also helium, all the gases show greater values for the coefficient of expansion than for the coefficient of pressure, and the differences are greater the greater the coefficient of expansion of the gas.

Since, as we have already stated, the law of Boyle is directly related to the law of Dalton, both being dependent on molecular movements, the same course of reasoning used to account for the variations in the case of Boyle's law applies equally to the case of Dalton's law. The "law" of Avogadro follows also as a necessary consequence of this explanation of the laws of gaseous pressure and temperature. If all gases show approximately the same increase in pressure when heated under constant volume, and if the increased pressure is due only to the increased energy with which the molecules strike the sides of the containing vessel, it follows that all gases must contain the same number of molecules in unit volume. But as, from the very nature of the case, the laws of Boyle and Dalton cannot be mathematically true, it follows that the laws of Avogadro and Gay Lussac must be only approximations in the same sense.

The law of Graham, connecting the rate of diffusion of a gas with its density, follows also as a necessary consequence of this explanation of the laws of Boyle, Dalton, Gay Lussac, and Avogadro. If the number of molecules in the unit volume of any gas, whatever be its nature and whatever be their mass, is approximately the same, it follows that the mean velocity of the molecules must be variable; their mean velocities must be in the inverse ratio of the square roots of their densities.

The mean velocity with which the molecules of a gas move can be calculated if we know the pressure it exerts, the weight of a definite volume, and the value of the acceleration due to gravity. The square of this velocity in metres per second of time at  $0^{\circ}\text{C}$ . is given by the expression  $U^2 = 3pg/q$ , in which

$p$ =pressure per square metre=10,333 kilograms ;  $g$   
 =the gravitation constant=9.81 ;  $q$ =weight of a cubic  
 metre of the gas at  $0^\circ$  C. and one atmosphere of  
 pressure.

For hydrogen we have  $U^2=3 \times 10,333 \times 9.81/0.0899$ ,  
 whence  $U=1,842$  metres per second ; for oxygen we  
 have  $U^2=3 \times 10,333 \times 9.81/1.430$ , whence  $U=461$ .  
 These numbers accord with those demanded by Graham's  
 law. The density of H being taken as 1, that of oxygen  
 is 16 and  $\sqrt{16}=4$  ; the numbers 1,842 and 461 are  
 in the ratio of 4 to 1.

The amount of heat required to raise the temperature  
 of the unit mass of a gas through a definite interval  
 depends, as Laplace first pointed out, upon whether the  
 gas is allowed to expand or not ; in other words, the  
 specific heat of a gas varies as the heating is at constant  
 volume or at constant pressure. If, having raised the  
 temperature of the unit mass, and so expanded it, we  
 then compress it until it occupies its initial volume, a  
 further rise of temperature takes place without any exter-  
 nal heat having been applied. This rise of temperature  
 is, in fact, due to the liberation of the amount of heat  
 required merely to expand the gas without increasing its  
 temperature. The quantity of heat needed to raise the  
 temperature of a gas through a definite interval is there-  
 fore greater when it is allowed to expand than when its  
 volume is kept constant ; in other words, the specific  
 heat at constant pressure is greater than the specific heat  
 at constant volume. The ratio of the two specific heats  
 can be calculated : on the assumption that the energy  
 imparted to the molecules simply accelerates their mean  
 rectilinear velocity, and that no energy is absorbed in  
 doing internal work among them, it is found that, when  
 the gas is permitted to expand, the amount of heat

required is 1.67 times greater than that needed when its volume is kept constant. This ratio has been experimentally determined for a number of gases. For oxygen under normal conditions it is 1.408, for hydrogen 1.414, for carbon dioxide 1.264, for methane 1.269—all numbers notably below the value 1.67. The direct experimental determination of this ratio by thermometric measurements is a matter of some difficulty. It was, however, demonstrated by Dulong that it can be ascertained with comparative ease from observations on the velocity of sound in the gas—the velocity being probably a direct function of this ratio. As carried out experimentally, the method consists in sending a sound wave through the gas contained in a glass tube, along the horizontal length of which is strewn a quantity of a light powder such as the spores of lycopodium or finely divided silica. The glass tube is fitted at one end with a glass rod; by rubbing this a series of longitudinal vibrations is set up and communicated to the gas whereby the light powder is thrown up into little heaps along the tube, the distance between the heaps being equal to half a wave length. By comparative measurements with air and the gas under examination, data are obtained from which the ratio of the specific heats can be deduced.

By experiments conducted on this principle Kundt and Warburg found that mercury vapour gave numbers agreeing with the theoretical ratio 1.67. Now, its vapour density shows that mercury-vapour is a monatomic gas; it actually fulfils the conditions prescribed for a gas which theory indicates should give the value 1.67. All the energy imparted to its molecules on heating simply accelerates their translational velocity. On the other hand, all the gases above

named as giving values below 1.67 are diatomic gases; in their case the energy imparted to them is employed partly in augmenting the translational velocity of the molecules, and partly in bringing about internal changes within them. By experiments made in like manner Ramsay and Travers succeeded in showing that the inert gases of the atmosphere are monatomic.

No attempt can be made here to explain the various methods by which it has been sought to obtain an estimate of the absolute size of gaseous molecules or to determine their number in a definite volume. By observations on their viscosity, rates of diffusion, conductivity for heat, variations from the law of Boyle, dielectric constants, electric charges, etc., Maxwell, O. E. Meyer, Loschmidt, Lothar Meyer, Van der Waals, Mossotti, Planck, Sir J. J. Thomson, and others, have arrived at estimates of the magnitude and number of molecules in a gas. These estimates necessarily vary with the hypotheses made in deducing them. It would serve no useful purpose to give the results, since the figures convey no impression to the mind of the minuteness of molecules, or even as to the extraordinary number of them in, say, so small a volume as one cubic centimetre. As an example, it has been calculated that there are about 640 trillions of hydrogen molecules in one milligram of the gas (O. E. Meyer, *The Kinetic Theory of Gases*, 1899).

In the preceding volume a short account has been given of the history of the early attempts to effect the liquefaction of the gases. These resulted in their division into the two classes of *liquefiable* and *permanent* gases. One of the most notable achievements of the latter half of the last century was to sweep away this

arbitrary distinction. The fundamental condition needed to effect the liquefaction of a gas, although surmised by Faraday, was first clearly indicated by Andrews about 1863. He showed that, in order to liquefy a gas, its temperature must be lowered to a point peculiar to each gas, when, on the application of sufficient pressure, it will become a liquid. Thus, in the case of gaseous carbon dioxide, Andrews found that, if its temperature were maintained above  $31^{\circ}\text{C.}$ , no amount of pressure would cause it to liquefy; if the temperature were lowered just below this point—termed the *critical point*—a pressure of 75 atmospheres would effect its liquefaction. On the other hand, if the temperature of the liquid carbon dioxide be slowly raised to about  $31^{\circ}$ , the surface of demarcation between the liquid and the gas becomes gradually fainter and eventually disappears. Carbon dioxide may thus be made to pass from the state of liquid to that of gas without any sudden alteration of volume. If a given volume of the gas, say at  $50^{\circ}$ , be exposed to gradually increasing pressure, say up to 150 atmospheres, the volume is gradually diminished with the increment of pressure, but no sudden contraction indicating liquefaction occurs. If the gas under the high pressure be allowed to cool down to the ordinary temperature, no sudden contraction is observed to follow. The carbon dioxide, at the outset a gas, in the end becomes a liquid by a gradual and continuous transition, unaccompanied by any abrupt change of volume. These observations show that what we style the liquid and gaseous states are simply separated manifestations of the same condition of matter. There is a definite temperature for every gaseous substance at which it ceases to be liquefiable under pressure; and the reason that Faraday failed to liquefy



certain gases was that he was unable, with the means at his command, to lower their temperatures sufficiently and so reach their critical points; hence the enormous pressures which he and other investigators applied were unavailing. These facts were definitely made known by Andrews in 1869, were theoretically developed by Van der Waals in 1873, and practically applied to the liquefaction of oxygen in 1877, independently and almost simultaneously, by Pictet, of Geneva, and Cailletet, of Chatillon-sur-Seine. Pictet exposed oxygen, under great pressure, to the cold produced by the rapid evaporation of liquid carbon dioxide; Cailletet brought about the same result by suddenly diminishing the tension of the strongly compressed oxygen, the rapid expansion of the gas effecting the reduction of its temperature below the critical point. Other workers took up the subject, notably Wroblewski and Olszewski in Poland, Dewar in England, and Kammerlingh Onnes in Holland; and the liquefaction of all the gases has now been accomplished.

The following Table shows the *absolute* boiling (B.P.) and melting points (M.P.), critical points (C.P.) and pressures (C.Press.), together with the density (D) at their boiling-points of a number of liquefied gases:—

	B.P.	M.P.	C.P.	C.Press.	D.
	<i>degrees</i>	<i>degrees</i>	<i>degrees</i>	<i>m.</i>	
Helium	4.5	—	—	—	0.15
Hydrogen	20	15	35	11.6	0.06
Oxygen*	90.5	below 50	154	44	1.131
Nitrogen	77.5	60	124	20.9	0.791
Methane	108.3	—	191	42.4	0.416
Ethylene	169.5	104	282	44	0.571
Fluorine	186	40	—	—	1.11
Chlorine	239.6	—	—	—	1.507
Ammonia	234.5	197.5	404	85.9	—

	B.P. <i>degrees</i>	M.P. <i>degrees</i>	C.P. <i>degrees</i>	C.Press. <i>m.</i>	D.
Neon	30.40	—	below 65	—	—
Argon	86.90	—	155.6	40.2	1.212
Krypton	121.33	—	210.5	41.2	2.155
Xenon	163.9	—	287.8	43.5	3.52

The principle of the Cailletet method of effecting the liquefaction of oxygen had been theoretically and experimentally studied by Joule and Lord Kelvin many years previously. It was extended by Siemens and has been applied by Linde and Hampson to the construction of machinery for the production of liquid air on a large scale, without the use of any intermediate refrigerant.

It is now readily possible to procure considerable quantities of liquid air, and even of liquid hydrogen. By the evaporation of liquid hydrogen temperatures approaching the *absolute zero*—that is,  $273^{\circ}$  C. below the melting-point of ice—can now be reached. Incidentally there has been developed a special field of inquiry relating to the behaviour of substances at low temperatures.

The pioneers in this field have been Dewar in England and Kammerlingh Onnes in Holland. Research at low temperatures, indeed, has been the main feature of the work of the Royal Institution of Great Britain during the last twenty years. It has included observations, at temperatures approaching the absolute zero, on the electrical resistivity of metals and alloys, on the behaviour of so-called insulators, on changes in the cohesive force of metals, on the dielectric constants of frozen electrolytes, on the influence of cold on magnetisation and on magnetic permeability, and on the optical behaviour of bodies, on vital phenomena at low temperatures, and on the influence of cold on chemical change.

Dewar has succeeded in liquefying and solidifying large quantities of hydrogen, and has studied its properties at low temperatures. Liquid hydrogen is transparent and colourless. It is a non-conductor of electricity, and gives no absorption spectrum. It freezes into an ice-like solid, devoid of metallic properties. Dewar has made use of the property possessed by charcoal of occluding gases, especially at low temperatures, in the production of high vacua, and in the separation of gases; and he has also determined the molecular heat of absorption by charcoal of various gases. He has employed liquid air, liquid nitrogen, and liquid hydrogen as calorimetric agents, and has determined by means of them the heat capacities of a number of substances at very low temperatures. Lastly, his ingenious contrivance of silvered vacuum protected vessels, now introduced into commerce under the name of "Thermos flasks," has greatly facilitated the manipulation of liquefied gases for experimental purposes.



SIR JAMES DEWAR.

## CHAPTER VI.

### THE PERIODIC LAW

IN an anonymous essay "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms," published in Thomson's *Annals of Philosophy* in 1815, the attempt was made to indicate certain consequences which seem to follow from Dalton's law of gaseous volumes, as generalised by Gay Lussac. The author of this essay was subsequently discovered to be a medical student named William Prout, noteworthy as having been one of the first to point out the suggestiveness of the numerical relationships which occur among the atomic weights of the elements. This paper is usually assumed to contain the statement that the atomic weights of the elements are multiples of that of hydrogen. As a fact, however, this hypothesis is nowhere explicitly stated in the paper. The inference was practically due to Thomson, who strove to support it by experimental proof of so weak a character as to draw forth the remark of Berzelius that much of it appeared to have been made at the writing-desk.

Nevertheless, the occurrence of such numerical relationships continued, as already stated, to excite speculation. Döbereiner, in 1829, pointed out that in certain groups of correlated elements, consisting each of three members, the middle member had an atomic weight practically identical with the arithmetic mean of the atomic weights of the others; and similar

observations were made by Gmelin, Dumas, Gladstone, and Strecker. An approach to the recognition of the general law underlying these facts was made by Newlands in England, and independently by De Chancourtois in France, who were the first to indicate that the properties of the elements are related to their atomic weights. This conception was developed by the Russian chemist, Mendeléeff. In Mendeléeff's arrangement, first published in 1869, the elements are so grouped that their properties are periodic functions of their atomic weights. The general statement of what is now known as the Periodic Law may be put in this form: If the elements are arranged in order of increasing atomic weight, the properties of these elements vary from member to member of the series, but return more or less nearly to the same value at certain fixed points in the series. This is observed to occur in the atomic value, or valency, of the several members; also in their specific volumes, melting points, ductility, hardness, volatility, crystalline form, thermal expansion, refraction equivalents, and conductivities for heat and electricity, in their magnetic properties and electro-chemical behaviour, and in their heats of chemical combination, etc.

The first chemist of note to grasp the significance of Mendeléeff's generalisation was Lothar Meyer, who, dealing at the outset with one of the characteristic properties of the elements—viz., their specific or atomic volumes (that is, the values obtained by dividing their specific gravities into their respective atomic weights)—greatly developed the principle of periodicity, representing it graphically in a most striking and suggestive manner, leading up to a classification almost identical with that of Mendeléeff.

Since the date of its promulgation the scheme of classification of the elements in accordance with the principle of periodicity has experienced certain minor modifications necessitated by fuller knowledge; but in its essential features it remains very much in the form devised by Mendeléeff. The discovery of the so-called inert and radio-active elements required that their relations to the periodic law should be defined. Their inclusion raises no fundamental difficulty. Indeed, the generalisation seems to adapt itself to the far-reaching considerations which spring from modern views of the nature of the atom, its electro-chemical relationships, and the orderly arrangement of the corpuscles of which it may be composed. In the 1905 edition of the English translation of his famous *Principles of Chemistry*, Mendeléeff has given a table which may be said to embody his final views concerning the systematic classification of the elements. This is reproduced on p. 83. In this table he postulates the existence of two hypothetical elements,  $x$  and  $y$ , the former of which he regards as identical with the physical ether; while the latter is an analogue of helium, possibly identical with the "coronium" of the solar coronal atmosphere, with a molecular weight of about 0.4.

The striking feature of Mendeléeff's generalisation is its universality. In this respect it differs from all previous attempts at natural classifications of the elements; these were limited and partial, and therefore unsatisfactory. Nevertheless, it is easy to trace in them fundamental conceptions upon which Mendeléeff built. Mendeléeff, in fact, gave a great extension to ideas with which the chemical world of half a century ago was more or less familiar; and doubtless it was to

Series.	Zero group.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
0 ..	—	Hydrogen, H = 1.008	—	—	—	—	—	—	—
1 ..	—	Lithium, Li = 7.03	—	—	—	—	—	—	—
2 ..	Helium, He = 4.0	Beryllium, Be = 9.1	Boron, B = 11.0	Carbon, C = 12.0	Nitrogen, N = 14.04	Oxygen, O = 16.0	Fluorine, F = 19.0	—	—
3 ..	Neon, Ne = 19.9	Magnesium, Mg = 24.1	Aluminium, Al = 27.0	Silicon, Si = 28.4	Phosphorus, P = 31.0	Sulphur, S = 32.06	Chlorine, Cl = 35.45	—	—
4 ..	Argon, Ar = 38	Potassium, K = 39.1	Scandium, Sc = 44.1	Titanium, Ti = 48.1	Vanadium, V = 51.4	Chromium, Cr = 52.1	Manganese, Mn = 55.0	Iron, Cobalt, Fe = 55.9 Co = 59 Ni = 59 (Cu)	Nickel, Ni = 59 (Cu)
5 ..	—	Copper, Cu = 63.6	Zinc, Zn = 65.4	Gallium, Ga = 70.0	Germanium, Ge = 72.3	Arsenic, As = 75.0	Bromine, Br = 79.95	—	—
6 ..	Krypton, Kr = 81.8	Rubidium, Rb = 85.4	Strontium, Sr = 87.6	Yttrium, Y = 89.0	Zirconium, Zr = 90.6	Niobium, Nb = 94.0	Molybdenum, Mo = 96.0	Ruthenium, Rhodium, Palladium, Ru = 101.7 Rh = 103.0 Pd = 106.5 (Ag)	—
7 ..	—	Silver, Ag = 107.9	Caesium, Cs = 132.2	Indium, In = 114.0	Tin, Sn = 119.0	Antimony, Sb = 120.0	Tellurium, Te = 127	Iodine, I = 127	—
8 ..	Xenon, Xe = 128	Caesium, Cs = 132.2	Barium, Ba = 137.4	Lanthanum, La = 139	Cerium, Ce = 140	—	—	—	—
9 ..	—	—	—	—	—	—	—	—	—
10 ..	—	—	—	Ytterbium, Yb = 173	—	Tantalum, Ta = 183.0	Tungsten, W = 184	—	Osmium, Iridium, Platinum, Os = 191 Ir = 193 Pt = 194.9 (Au)
11 ..	—	Gold, Au = 197.2	Mercury, Hg = 200.0	Thallium, Tl = 204.1	Lead, Pb = 206.9	Bismuth, Bi = 208	—	—	—
12 ..	—	—	Radium, Ra = 224	—	Thorium, Th = 232	—	Uranium, U = 239	—	—



this circumstance, combined with the remarkable boldness and comprehensiveness of this extension, followed almost immediately by a most striking series of confirmations of his own previsions, as logical consequences of his generalisation, that secured for it attention, and ultimately universal adoption.

The periodic law, in the words of its author, is the "direct outcome of the stock of generalisations of established facts which had been accumulated by the end of the decade 1860-1870." It is founded wholly on experiment, and is as much the embodiment of fact as are the laws of chemical combination. It was based upon the adoption of the definite numerical values of the atomic weights, as indicated by Cannizzaro, as a consequence of the hypothesis of Avogadro, and upon the assumption that the relations between the atomic weights of analogous elements must be governed by a general law. The application of the periodic law immediately led to the re-determination of certain atomic weights, and to the correction of their assumed atomic values. At the time of its enunciation the determination of the valency of an element was purely empirical, with no apparent necessary relation to that of other elements. We find now that the valency is a matter of *à priori* knowledge, just as much as any other property of the element. The amended values for the atomic weight and valency of a number of elements thus demanded by the law have been confirmed by all the experimental criteria employed by chemists. The generalisation further indicated the existence of new elements; it pointed out their probable sources, and foretold their properties. Instances of this power of divination in the law are to be seen, as already mentioned, in the discovery of *gallium* by Lecoq de

Boisbaudran, of *scandium* by Nilson, and of *germanium* by Winkler, the existence and main properties of which were severally foretold by Mendeléeff in 1871.

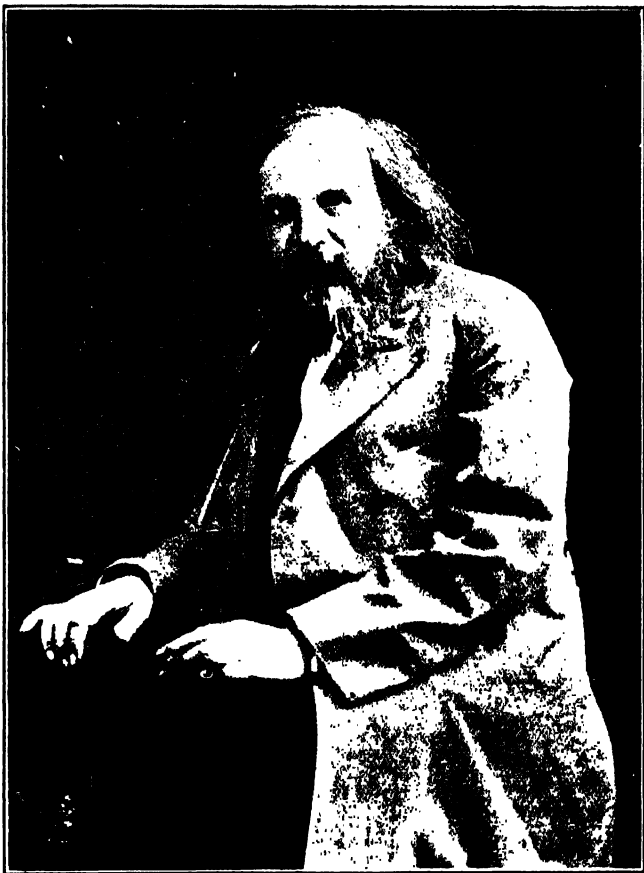
The promulgation of the law was heralded as a proof of the validity of the conception of a primordial matter. It was held that it can find a rational explanation only in the idea of unity in the formative material. But its author would not admit that his generalisation had any relation to the Pythagorean hypothesis :—

The periodic law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements. It does not in the least originate in the idea of an unique matter, and it has no historical connection with that relic of the torments of classical thought ; and therefore it affords no more indication of the unity of matter or of the compound nature of the elements than do the laws of Avogadro and Gerhardt, or the law of specific heats, or even the conclusions of spectrum analysis. None of the advocates of an unique matter has ever tried to explain the law from the standpoint of ideas taken from a remote antiquity, when it was found convenient to admit the existence of many gods—and of a unique matter.

The reader who desires a fuller exposition of the principles of the periodic law must be referred to special treatises on the subject, or to the larger manuals on general chemistry. It must, however, be stated that, while many facts discovered since the original promulgation of the principle and since its development by Lothar Meyer, Carnelley, Thomsen, and others, are consistent with the law, other facts, some of which were known before 1870, are apparently out of harmony with it, or at all events await a fuller interpretation. For example, tellurium is not

in its proper place in the scheme if its atomic weight, 127.5, has been correctly ascertained. Cobalt (58.97) and nickel (58.68) have atomic weights so closely accordant that their properties and those of their corresponding compounds should be very similar, and, in fact, almost identical; but such is not the case. Indeed, it has been said, no prevision of the periodic law would have led to the discovery of nickel. Similar considerations apply to manganese, chromium, and iron; the atomic weights of these elements are less widely different than the differences in their properties and the divergence in their chemical relationships would seem to require. The relative positions of argon and potassium are also not consistent with the law. There are difficulties, too, connected with what we know at present concerning the atomic weights of the so-called rare earth metals. In spite, however, of these seeming anomalies, it can hardly be doubted that the periodic law is as much the expression of a natural law as is the law of gravitation; although it is possible, and indeed probable, that, as we now define it, it is only the first approximation to the truth, and that, as our knowledge becomes more precise, Mendeléeff's classification, in its present form, will require modification and extension, just as Mendeléeff's own scheme may be said to be a modification and extension of the attempts at the rational classification of the chemical elements made by his predecessors.

**Dmitri Ivanowitsch Mendeléeff**, with whose name this fruitful generalisation is indissolubly connected, was born February 7th, 1834 (N.S.), at Tobolsk, in Siberia, and was the fourteenth and youngest child of Ivan Mendeléeff, the Director of the gymnasium at that place. Soon after the birth of Dmitri his



DMITRI IVANOWITSCH MENDELÉEFF.

father became blind, and the family were practically dependent upon the mother, Maria Dmitrievna Mendeleeva, who established a glass works near Tobolsk, on the profits of which she brought up and educated her large family. At the age of fifteen Mendeléeff was taken by his mother to St. Petersburg, and began the study of natural science at the Physico-Mathematical Faculty of the Institute. After serving as a science master at Simferopol in the Crimea and at Odessa, in 1856 he became a *privat-docent* in the university; then, following a short period of study in France and Germany, he returned to St. Petersburg, and in 1866 he was made Professor of General Chemistry in the university. His reputation mainly rests upon his contributions to chemical philosophy and physical chemistry, notably on specific volumes, on critical temperatures, on the thermal expansion of liquids, on the nature of solutions, on the elasticity of gases and the origin and nature of petroleum. He died on January 31st, 1907.

## CHAPTER VII.

### VALENCY

CHEMICAL formulæ, from the time of Berzelius onwards, have been regarded as rational expressions—that is, they serve to represent the relations and analogies of the substance they are employed to designate, and indicate in the simplest and at the same time the most comprehensive manner the chemical changes in which the substances take part. In the words of Gerhardt, those formulæ are “the best that make evident the greatest number of such relations and analogies,” and that serve to express the greatest number of the chemical changes in which they are concerned.

In such concrete expressions of chemical change it was frequently observed that a definite group of some or all of the constituent elements of the substance hung together, as it were, and passed, apparently unchanged, into the products of its transformation. These groups were not necessarily radicals in the sense in which Liebig and Wöhler used the term; to Gerhardt and to Kekulé they were simply *residues*, remaining unattacked in a chemical metamorphosis, and passing as such into the products of the change. They might or might not be capable of isolation as definite entities. Thus, for example, we may represent the composition of the following sulphur compounds so as to show that they all contain the group  $\text{SO}_2$ , or *sulphuryl*:—

$\text{SO}_2 \left\{ \begin{array}{l} \text{Cl} \\ \text{Cl} \end{array} \right.$		$\text{SO}_2 \left\{ \begin{array}{l} \text{Cl} \\ \text{OH} \end{array} \right.$
Sulphuryl chloride.		Chlorosulphonic acid.
$\text{SO}_2 \left\{ \begin{array}{l} \text{NO}_2 \\ \text{Cl} \end{array} \right.$	$\text{SO}_2 \left\{ \begin{array}{l} \text{NO}_2 \\ \text{OH} \end{array} \right.$	$\text{SO}_2 \left\{ \begin{array}{l} \text{OH} \\ \text{OH} \end{array} \right.$
Sulphuryl nitryl chloride.	Leaden chamber crystals.	Sulphuric acid.

These formulæ serve to show how the several substances are mutually related, and that they may be derived from one another by the substitution of atoms of chlorine for hydroxyl (OH), or nitryl (NO<sub>2</sub>), or *vice versa*.

It was pointed out in 1851 by Williamson, and subsequently by Gerhardt, that these groups are characterised by differences in their power of combining with or replacing atoms of hydrogen, or of groups or elements which, like chlorine, are chemically equivalent to hydrogen. Such a radical or residue as *ethyl* (C<sub>2</sub>H<sub>5</sub>) is chemically equivalent to *one* atom of hydrogen, as is shown when we compare the formula for ether, as established by Williamson, with that of ordinary alcohol :—



*Sulphuryl*, SO<sub>2</sub>, is chemically equivalent to *two* atoms of hydrogen; *phosphoryl*, PO, as suggested by Odling, to *three* atoms of hydrogen. Gerhardt therefore proposed to designate these and similar groups as *mon-atomic*, *diatomic*, *triatomic*, according to their respective hydrogen replacing power.

This conception of the definite atom-fixing or replacing power of groups or compound radicals was extended by Frankland, in 1852, so as to include the simple radical—that is, the elements. In the memoir

in which he announced the existence of the organo-metallic compounds he pointed out that the elements may be classified according to their combining power, or, as he expressed it, according as "their affinities are best satisfied." This idea was independently developed by Couper and Kekulé in 1858; it is from that period that the definite introduction of the conception of *atomicity*, *atomic-value*, or *valency*, into chemical doctrine may be said to date.

The memoir in Liebig's *Annalen der Chemie und Pharmacie*, in which Kekulé announced his views, deals particularly with the tetravalency of carbon and the doctrine of linking of atoms in terms of their valency. As formulated by Kekulé and as subsequently developed in his famous text-book, this doctrine exercised an immediate effect on the progress of the chemistry of carbon compounds. Like every fruitful hypothesis, it stimulated inquiry, and brought out analogies; and the more it was applied the more apparent became its suggestiveness and utility. The scope of chemical formulæ was greatly extended. Rational formulæ grew into dissected or constitutional formulæ; and on the system of constitutional formulæ have been grafted successive attempts to elucidate the manner in which the constituents of a molecule are grouped and held together. It is interesting to note that the proximate effect of the theory of chemical structure which grew out of Kekulé's doctrine was to assimilate what was sound in the seemingly antagonistic theories of types and radicals. As a mode of exposition, Kekulé used models to illustrate the manner in which the affinity-values of compounds are satisfied; these were not intended to represent the actual spatial distribution of the atoms in a molecule, but they nevertheless familiarised the



mind with the idea first clearly recognised by Wollaston and Berzelius that this is the ultimate aim of chemistry. It was probably their use, either actually or by visualisation, that led Kekulé in 1865 to his theory of the constitution of benzene, as developed in his paper on the constitution of the aromatic compounds—a theory no less fruitful in its consequences than that of the tetravalency of carbon and of the linkage of atoms. Such models, too, in the hands of Van 't Hoff, subsequently served to elucidate the connection between optical characters and crystalline form, and to explain the isomerism of certain organic substances.

Kekulé was of opinion that the valency, or affinity-value, of an element was a definite and invariable quantity—a fundamental property of the atom as immutable as its atomic weight. Many facts appear to show that such is not the case. Thus phosphorus and nitrogen are sometimes trivalent and at other times pentavalent; tin, in certain of its compounds, is divalent; in others, tetravalent. Sulphur may be a dyad, a tetrad, or a hexad. It will be seen that the valency of these particular elements varies by two units: this was at one time held to be a natural law, and the various elements were divided by Frankland into the two main groups of (1) *perissads*, or elements of odd atomic value, and (2) *artiads*, or elements of even atomic value. Experience has demonstrated that a rigid classification on this basis is not possible. Many instances are known of elements not only varying in valency by two units, but even by one unit. Thus nitrogen, which is usually a *perissad*, is apparently an *artiad* in nitric oxide and in gaseous nitrogen peroxide. Roscoe has shown that uranium and tungsten, originally regarded as *artiads*, form pentachlorides.

To what the difference in the affinity-value of an element is due, and why different elements should manifest different values, is at present unknown. Valency, like other properties, appears to be a periodic function of atomic weight; from the behaviour of such analogous compounds as phosphorus pentafluoride, phosphorus pentachloride, phosphorus pentabromide, it seems, too, to be related to the weights of the atoms in combination. Further, it would appear that the mutual affinities of substances vary with temperature—*i.e.*, with the energy imparted to their molecules; numerous instances appear to indicate that the atom-fixing power of an element decreases when it is strongly heated—that is, when the internal energy imparted to its combinations exceeds a certain limiting value. Van 't Hoff has attempted a mechanical explanation of valency depending on the shape of the atoms, as affected by variation in their vibratory motions resulting from differences of temperature. Helmholtz suggested that the different charges of electricity associated with the atoms may determine their affinity-values—that, for example, a monad carries a single charge, a dyad two, a triad three charges. Many considerations go to show that the affinity value of an element is not capable of definite numerical expression in the sense which the doctrine of valency as generally understood implies, and that the variations are not of the *per saltum* character assumed by saying that the affinity-value is sometimes 1, sometimes 2, at other times 3, and so on. When we have apparently satisfied the accepted atomic value of an element by allocating to it what we regard as the necessary complement of atoms of other bodies, it is frequently evident that the capacity for combination of the whole

molecule is not satisfied. Many apparently saturated molecules have the power of combining with other equally saturated molecules. Sulphur trioxide ( $\text{S}\text{O}_3$ ) and barium monoxide ( $\text{BaO}$ ) would appear each to have their affinity values satisfied; nevertheless, they combine with great readiness to form barium sulphate,  $\text{BaSO}_4$ .

## CHAPTER VIII.

### THE CHEMISTRY OF AROMATIC COMPOUNDS

THE suggestions of Couper and Kekulé that an explanation of the properties of chemical compounds should be sought in the nature and mutual affinities of their constituent elements rather than of their radicals were not wholly accepted at the time they were first made. Speculative ideas have to justify themselves by facts. The value of an hypothesis depends upon its usefulness and expediency, and on its power of indicating the lines of future inquiry. How far it is inductively sound and deductively useful is a matter for individual judgment. Consequently the tendency to pass from purely rational and constitutional formulæ to formulæ which sought to symbolise the inner structure—the very skeleton, as it were—of a molecule, was resisted for a time, and by no one more strongly than by Kolbe.

Kolbe's attitude to the new doctrine may be said to have had its justification in his own work. His remarkable prediction, based on considerations which had nothing in common with Kekulé's doctrine, of the existence of the secondary and tertiary alcohols, so soon to be confirmed by Friedel's discovery of secondary propyl alcohol, and by Butlerow's isolation of tertiary butyl alcohol, served to retard the general adoption of Kekulé's views by showing that apparently they were no more fruitful in suggestiveness than those they were intended to supplant. But it was exactly in

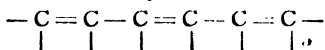
their suggestiveness with regard to the development of isomerism that structural formulæ based upon valency were gradually found to be most useful. It was perceived that it was now possible not only to foretell the existence of isomers, but to determine their number, and to some extent to forecast their properties and modes of decomposition. Cayley, for example, calculated the number of possible isomers of the hydrocarbons of the generic formula  $C_n H_{2n+2}$ ; and up to  $C_6H_{14}$  all those that theory predicted have been discovered. In no single case have more been obtained than the number indicated by theory. The accumulated weight of this and similar testimony ultimately established the doctrine of chemical structure on a firm basis.

This conception received a great extension as the result of Kekulé's application of his ideas to the explanation of the chemical constitution of the group of substances of vegetable origin—consisting of essential oils, balsams, resins, and their products, which, on account of their characteristic odours, were collectively known to the older chemists as the *aromatic compounds*. Some of these, like oil of bitter almonds, gum benzoin, coumarin, oil of wintergreen, oil of anise, oil of cinnamon, oil of cumin, balsam of tolu, phenol, and certain of their derivatives, such as benzene, aniline, salicylic acid, cinnamic acid, toluene, cymene, had already been investigated with important theoretical results; but as a class they had received far less attention than the derivatives of the great group of homologous radicals of which methyl is the initial member. Of course it was part of the doctrine of Liebig—the discoverer of benzoyl—that the aromatic compounds also contained specific radicals; but the relation of these compounds to those we now call aliphatic (fatty)

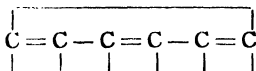
compounds was not understood, although certain analogies were recognised.

In 1866 Kekulé drew attention to the following significant peculiarities of the aromatic compounds: (1) All aromatic compounds, even the simplest, are comparatively richer in carbon than the corresponding class of fatty (aliphatic) compounds; (2) among the aromatic substances, as among fatty compounds, numerous homologous compounds exist; (3) the simplest aromatic substances contain at least six atoms of carbon; (4) all decomposition products of aromatic substances show a certain family resemblance; the main product of the decomposition contains at least six atoms of carbon — *e.g.*, benzene  $C_6H_6$ , phenol  $C_6H_6O$ , etc., which would seem to indicate that all aromatic substances contain a nucleus or atomic grouping containing six carbon atoms. Within this nucleus the carbon atoms are in closer connection or denser combination, from which it follows that all aromatic compounds are comparatively rich in carbon. More carbon atoms can then be added to this nucleus according to the same laws that govern the fatty compounds. In this way the existence of homologous compounds may be explained.

On the assumption that carbon is tetravalent and that its valency is constant, Kekulé showed how, by linking together six carbon atoms by alternate single and double bonds, six affinity units may be left free. If we assume that six carbon atoms are attached to one another according to this law of symmetry, we obtain a group which, regarded as an *open chain*, contains *eight* unsaturated units of affinity:—



By making the further assumption that the two carbon atoms at the ends of the chain are linked together by one unit of affinity each, a *closed chain* (a symmetrical ring) is obtained which now contains *six* unsaturated units of affinity:—



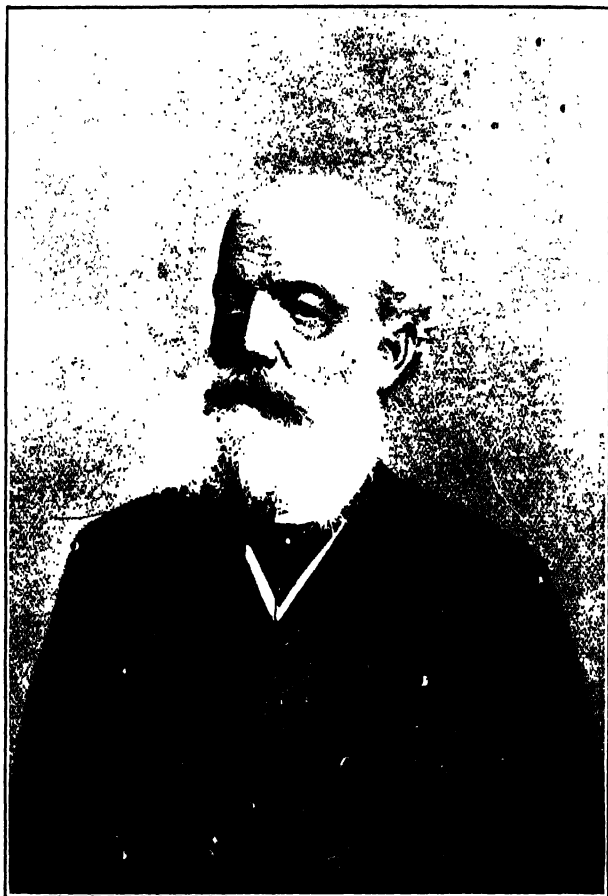
From this *closed chain* all the substances usually designated as "aromatic compounds" are derived. In these a common nucleus may be assumed: it is the closed chain  $C_6A_6$ , where A denotes an unsaturated affinity. The six affinities of this nucleus may be satisfied by six monovalent elements. They may also, wholly or in part, be satisfied by one affinity of polyvalent elements, the latter necessarily bringing with them other atoms into the compound, thus producing one or more side chains, which in their turn may be lengthened by the addition of other atoms.

If each of the free units is satisfied by an atom of hydrogen, we obtain benzene, which, as Kekulé demonstrated, becomes the centre round which the great group of aromatic compounds might be said to revolve. Benzene was discovered by Faraday in 1825 among the volatile liquids condensed from the oil-gas made by the Portable Gas Company. It had already played a notable part in the development of chemical theory in connection with the discovery of isomerism. It was now to play a far more important rôle: to become, in fact, the progenitor of a great family of substances, not only of theoretical value, but of great economic importance.

The limits of this work preclude any attempt to trace in detail the development of the conception with which

Kekulé enriched science, or to dilate upon the great extension of benzenoid or cyclic chemistry which has resulted from it during the past forty years. It has been said that Kekulé's memoir on the benzene theory is the most brilliant piece of scientific prediction to be found in the whole range of organic chemistry. Of course, on its promulgation it had to run the gauntlet of criticism; and an army of eager, active workers was soon engaged in testing its sufficiency and in developing the rich province which it first made known. As the facts multiplied, other statical formulæ were suggested by Dewar, Ladenburg, and Claus, but they have not proved more adequate to explain the facts as these have become better understood. Observations which seemed to contradict Kekulé's theory, or which seemed to be imperfectly explained by it, have, in the light of fuller knowledge, been shown to be in harmony with it; and such additional proofs of agreement have thereby served to strengthen its position. Its capacity for development is, indeed, as in the case of every other hypothesis of the first rank, one of its cardinal qualities. It adequately explains the constitution of great numbers of derivatives whose analogies and relations, apart from its, would have remained obscure and in many cases unintelligible. The symmetrical distribution of the carbon and hydrogen atoms in the benzene molecule, assumed by Kekulé on indirect grounds, has been established by the independent investigations of Ladenburg and others, and its ring structure has been demonstrated by Baeyer and Perkin. Purely physical evidence, based upon its thermo-chemical and optical characters, can be adduced in its support. Determinations of the molecular volume and magnetic rotation of its compounds further serve to substantiate it.





AUGUST KEKULE VON STRADONITZ.

**Friedrich August Kekulé** was born at Darmstadt on September 7th, 1829. After passing through the gymnasium of his native town, he entered, in 1847, the University of Giessen, with the intention of becoming an architect. Attracted by Liebig's teaching, he turned to chemistry, and worked with Will on *amyl sulphuric acid* and its salts. In 1851 he went to Paris, heard Dumas's lectures, and formed a friendship with Gerhardt, whose *Traité de Chimie Organique* largely moulded his views. He became an assistant to Von Planta, occupying himself with the chemistry of the alkaloids. Subsequently he came to London, worked under Stenhouse, and made the acquaintance of Williamson, then in the full vigour of his scientific activity. Here he discovered *thioacetic acid*. It was at this time, also, that his ideas with regard to structural chemistry began to take shape. Returning to Germany, he attached himself to the University of Heidelberg as a *privat-docent*, and had for a pupil Baeyer, who took up the study of the organo-arsenic compounds. In 1858 he published his memorable paper "On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon," in which he developed his views on the linking of atoms, out of which has grown our system of constitutional formulæ. The immediate result of this celebrated memoir was a call to the chemical chair of the University of Ghent, where Kekulé had among other students Baeyer, Hübner, Körner, Ladenburg, Linnemann, and Dewar. Here he remained nine years, and here he published his classical *Lehrbuch der Organischen Chemie*. The years he spent in Ghent were the most productive time of his career, and it was there that he developed his benzene theory—a conception as fruitful as that of his doctrine

of atom-linking. In 1867 Kekulé was called to Bonn to take charge of the newly erected laboratory which Hofmann had designed. Although he continued to work, mostly in collaboration with his pupils, among whom may be named Anschütz, Bernthsen, Thorpe, Carnelley, Claisen, Dittmar, Franchimont, Van 't Hoff, Japp, Schultz, Wallach, and Zincke, his health after 1876 began to fail. He died on July 13th, 1896.

Of course no statical formula can be the ultimate representation of the constitution of benzene. However convenient and suggestive such a formula may be, it can be only a transitional phase in its complete chemical and physical history. Kekulé was early conscious of this fact, and suggested a dynamical hypothesis based upon a mechanical conception of valency. This he imagined might represent the number of contacts with other atoms which a vibrating atom experienced in the unit of time. Two atoms of tetravalent carbon, each linked by one combining unit, will experience four oscillations, striking each other and three other atoms in the unit of time, while the monovalent hydrogen atom makes only one oscillation. The doubly linked carbon will collide with its neighbouring atom twice, and also with two other atoms within the same period. The assumption that the carbon atom has a more rapid motion than the hydrogen atom is, however, not warranted by the kinetic theory. Other dynamic formulæ have been proposed by Knorr and by Collie. Collie and Baly have further suggested that the absorption bands of benzene observed in the ultra violet of its spectrum point to synchronous oscillations of its molecule due to dynamic changes in the making and breaking of the links between the several pairs of

the carbon atoms, setting up vibrations in the benzene ring comparable with those of an elastic ring in the act of expanding and contracting.

The large group of the *essential oils*, containing hydrocarbons similar to oil of turpentine, and classed under the generic term of *terpenes*, might, from their origin and mode of occurrence, be expected to be allied in constitution to the aromatic compounds; and such is found to be the case. The terpenes are isomeric hydrocarbons of the formula  $C_{10}H_{16}$ . They are found sometimes singly, at other times mixed, in a great variety of plants, associated with *sesquiterpenes*  $C_{15}H_{24}$ , and oxygenated substances, such as camphor, borneol, menthol, etc., some of which have long been known and valued for their medicinal properties and technical applications. The elucidation of their constitution has taxed the skill of many workers during the past thirty years; but, thanks to the labours of Wallach, Baeyer, Perkin, Tiemann, Bredt, Komppa, and others, an insight has been gained into their nature and analogies. They are apparently all cyclic compounds with certain attributes which connect them with hydrocarbons of the aliphatic series. *Pinene*, the characteristic constituent of oil of turpentine, obtained by distilling the resinous exudations of many species of pines, exists in two modifications, distinguished by differences in optical activity, known respectively as *australene*, found in American, Russian, and Swedish turpentine, and *terebenthene*, found mainly in French turpentine. It would seem from their empirical formulæ, as well as from their association in nature, that the terpenes and *camphor*, which Dumas first showed to have the composition  $C_{10}H_{16}O$ , should be closely allied in

constitution, and that it ought to be readily possible to effect their mutual transformation. The constitution of camphor was long one of the standing problems of organic chemistry, and dozens of formulæ have been suggested at various times during the last twenty years in explanation of its structure. That it contained a benzene nucleus seemed to be proved by the ease with which it yielded toluene, cymene, and other benzene homologues. The first real insight into its structure was gained when Bredt ascertained the constitution of *camphoronic acid*,  $\text{C}_6\text{H}_{11}(\text{CO}_2\text{H})_4$ —a product, together with *camphoric acid*, of the oxidation of camphor—which he found broke up into trimethylsuccinic acid and *isobutyric acid*, and the structure of which was established by Perkin and J. F. Thorpe.

The result of the Japanese monopoly has been to greatly enhance the price of natural camphor; during the last ten years it has practically trebled. This has naturally stimulated endeavours to prepare this substance by synthetical means. *Artificial camphor* is now made from *pinene* by transforming the hydrocarbon into bornyl chloride by the action of hydrochloric acid. From this *camphene* is prepared; by treatment with glacial acetic acid it forms *isobornyl acetate*. On hydrolysis this is transformed into *isoborneol*, which by oxidation yields *camphor*, differing from the naturally occurring variety only in the fact that it is optically inactive. All so-called aromatic compounds are not necessarily cyclic systems, for it has been recognised within the past few years that some of the most valuable natural perfumes, such as that of the rose, lavender, and orange blossom, lemon-grass, geranium, ylang-ylang, neroli, etc., owe their characteristic aroma to the presence of terpenes and camphors, which are

not strictly benzenoid or cyclic compounds, but "ruptured rings" behaving like open-chain or aliphatic substances. To judge from past experience, it may be confidently stated that, now the constitution of these substances is understood, their synthetical preparation on an industrial scale is practicable. The discovery by Cahours in 1844 that *oil of wintergreen* is substantially methyl salicylate led to its artificial production from synthetically prepared salicylic acid. Sir William Perkin in 1868 effected the synthesis of *coumarin*, the aromatic principle in woodruff and hay. Fittig and Mielck in 1869 synthesised *heliotropin*, and in 1871 Tiemann and Haarmann obtained *vanillin*, the characteristic aromatic body in the vanilla pod, by synthetic means, and established its manufacture on a commercial scale. The chemical nature of the characteristic odoriferous substances in oil of cumin, anise, rue, cinnamon, heliotrope, jasmine, violet, parsley, etc., has now been established, and some of them are made industrially. The artificial essence of violets known as *ionone*, prepared by Tiemann in 1893, and now made commercially, is similar but not identical in structure with the true perfume—*irone*. What is known as *artificial musk* is a trinitro-butyl toluol. *Artificial orange-flower oil* is a methyl ester of anthranilic acid.

In Vol. I. a short account has been given of the early history of the large and important group of vegetable products known as the *alkaloids*. Many of these have long been valued on account of their powerful physiological action. As they all contain nitrogen and are generally basic, they were regarded by Berzelius, and subsequently by Liebig and Hofmann, as akin to ammonia in constitution, and were classed as amines. The first experimental evidence of their nature was

obtained by Gerhardt, who found that, when strychnine and certain of the alkaloids belonging to the quinine group are treated with potash, an oil was obtained which he termed *quinoline*, and which was recognised by Hofmann as identical with a substance obtained in 1834 from coal-tar by Runge, and at that time known as *leucol*. By other modes of treatment certain alkaloids—*e.g.*, nicotine and conine—are found to yield pyridine, a basic substance found by Anderson, in 1846, in the foetid liquor obtained by distilling bones, and since found in coal-tar. Others of them—*e.g.*, papaverine, narcotine, etc.—yield *iso-quinoline*, an oil also discovered in coal-tar, by Hoogewerff and Van Dorp, in 1885. These three substances—quinoline, *iso-quinoline*, and pyridine—constitute so many nuclei in the constitution of a large number of alkaloids. Pyridine resembles benzene in being a cyclic compound, consisting of five carbon atoms and one nitrogen atom. Quinoline stands to pyridine in much the same relation that naphthalene stands to benzene. It can be obtained synthetically, as first shown by Koenigs and Skraup, and subsequently by Doebner and Von Miller, from benzene derivatives.

*Iso-quinoline*, isomeric with quinoline, differs from that substance in the position of the nitrogen atom. It, too, has been synthetically prepared from benzene derivatives in a number of ways.

Among the naturally occurring pyridine alkaloids may be named *piperine*, found in black pepper, and *conine*, the poisonous principle of hemlock (*conium maculatum*). The latter alkaloid was prepared synthetically by Ladenburg in 1886; as first obtained it differed from the naturally occurring product, which is dextro-rotatory, in being optically inactive. Ladenburg

surmised that the synthetic preparation stood to the naturally occurring compound in the same relation that racemic acid stood to tartaric acid, and that, by treatment in the manner employed by Pasteur, the racemic modification of conine might be separated into its dextro- and lævo- constituents. This was found to be the case; but the separated dextro component was now found to be distinctly more optically active than the pure, natural variety. It was, in fact, an isomeric modification—*iso*-conine. By heating this to 300° it was transformed into ordinary conine, identical in all respects with the natural alkaloid. Ladenburg has also effected the synthesis of piperine by condensing piperidine and piperinic acid.

*Nicotine*, the alkaloid of tobacco, was discovered by Posselt and Reimann in 1828. Its constitution was first ascertained by Pinner, and it was synthetically obtained by Amé Pictet, in 1904, as an inactive substance, capable of being resolved by the crystallisation of its tartrates into a dextro- and lævo- modification, the latter of which was identical with that found in the tobacco leaf.

*Atropine* and *hyoscyamine*—the poisonous principles of belladonna and henbane—are isomeric alkaloids, the former of which is optically inactive, and the latter is lævo-rotatory. Atropine is, in fact, the racemic modification. The constitution of both alkaloids is known, and their synthesis is now possible.

The successive steps may be thus indicated:—

1. *Synthesis of glycerin* (Faraday, Kolbe, Melsens, Boerhave, Friedel, and Silva).

2. *Glycerin to glutaric acid* (Berthelot and De Luca, Cahours and Hofmann, Erlenmeyer, Lermantoff, and Markownikoff).



3. *Glutaric acid to suberone* (Brown and Walker, Boussingault).

4. *Suberone to tropidine* (Willstätter).

5. *Tropidine to tropine* (Willstätter, Ladenburg).<sup>3</sup>

6. *Synthesis of tropic acid* (Berthelot, Fittig and Tollens, Friedel, Ladenburg and Rügheimer).

7. *Tropine and tropic acid: atropine* (Ladenburg).

The alkaloid *cocaïne*, contained in the leaves of *erythroxylon coca* and now employed as a local anæsthetic, was discovered by Niemann in 1860. It has been shown to be closely related to atropine in constitution, and has now been synthetically prepared in the dextro-modification.

The alkaloids *papaverine*, *narcotine*, *narceïne*, contained in opium, are derivatives of *iso-quinoline*, as also is *berberine*, found in the common barberry (*berberis vulgaris*). Papaverine, which occurs in opium to the extent of about one per cent., was first isolated by Merck in 1848. Its constitution has been established by Goldschmiedt. *Narcotine* is, next to morphine, the most abundant constituent of opium. The study of the products of its hydrolysis and oxidation—viz., *opiunic acid* and *cotarnine*, both of which substances have long been known—has indicated its probable structure. *Narceïne* is closely allied to narcotine, and can, indeed, be obtained from it by combining the latter alkaloid with methyl iodide and treating the compound with caustic potash. The constitution of *berberine*, which is one of the few coloured vegeto-alkaloids known, has been worked out by Perkin. As yet nothing definite is known concerning the structure of the most important and largest constituent of opium—viz., *morphine*; or of its congeners *codeïne* and *thebaine*. Grimaux, however, in 1881 converted morphine into codeïne by treatment

with methyl iodide and potash ; hence the two alkaloids stand in a relation somewhat similar to that in which narceïne stands to narcotine. There is very little doubt that the three alkaloids are very closely related, and that a knowledge of the constitution of one of them would immediately elucidate the structure of the others. They are probably phenanthrene derivatives.

*Quinine* and *cinchonine*, the most important of the cinchona alkaloids, are quinoline compounds, and are closely related in constitution. But the many attempts to unravel their structure have yielded no definite results up to the present.

## CHAPTER IX.

### STEREO-ISOMERISM : STEREO-CHEMISTRY

THE first gropings in the search for light on the inner structure of molecular groupings may be said to date from Biot's work on polarisation. In 1815 Biot, a pupil of Malus, made the remarkable discovery that a number of naturally occurring organic compounds—*e.g.*, sugar, tartaric acid, oil of turpentine, camphor, etc., are *optically active*—that is, rotate the plane of polarisation in one direction or the other. The property had previously been observed in quartz, and was assumed to be connected with the crystalline character of that substance. Biot, however, pointed out that the case of oil of turpentine, which is a liquid, and the cases of the other substances when in solution, showed that crystalline character had no necessary connection with the phenomenon, but that it must be dependent upon the internal or molecular arrangement of the optically active substance.

In 1844 Mitscherlich, who first demonstrated the relation between atomic constitution and crystalline form, drew attention to the fact that the salts of the isomeric modifications of tartaric acid, studied by Berzelius, although possessing the same chemical composition, the same crystalline form, with the same angles, the same double refraction, and therefore the same angles between their optical axes, nevertheless behave quite differently as regards their optical activity, solutions of the tartrates rotating the plane

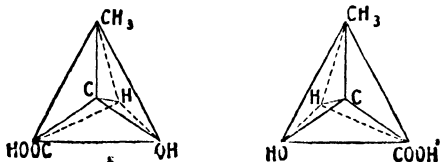
of polarisation, whereas those of the racemates are inactive. In 1848 this remarkable circumstance engaged the attention of Louis Pasteur, a young man who had just completed his course at the École Normale in Paris, and was acting as assistant to Balard, the discoverer of the element bromine. Pasteur, on examining the crystals of the two forms of tartaric acid, and of some of their salts, detected the presence, on some of them, of certain facets—so-called hemihedral faces—which had hitherto been unrecognised, but were similar to facets which Haüy had observed on quartz. Haüy had, in fact, divided quartz crystals into two classes—right-handed and left-handed, depending upon the side on which these facets occurred. The forms were, as it is termed, enantiomorphous. Biot, moreover, found that some quartz crystals, cut parallel to the axis, turned the plane of polarisation to the right, whereas others turned it to the left; and Herschel suggested that the phenomena were probably connected, and such was found to be the case.

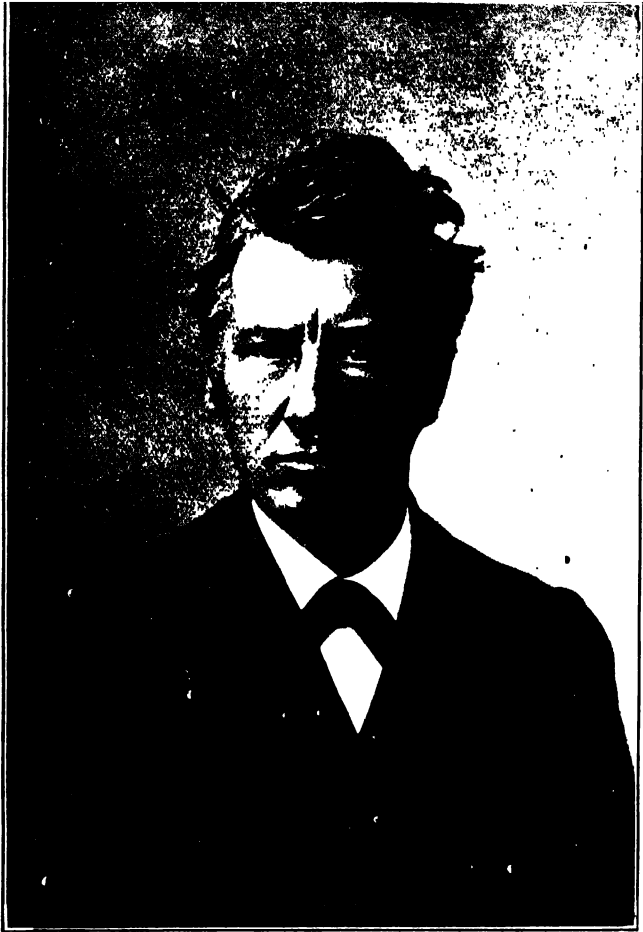
Mindful of Herschel's observation, Pasteur found that the crystals of certain of the optically active tartrates showed hemihedral faces, whereas those of the corresponding racemates showed no trace of them. On recrystallising the racemates, however, it was noticed that two sets of crystals were formed—enantiomorphic forms—the first set of crystals having hemihedral forms on the right-hand side, and the second set on the left-hand side. The forms, in fact, were so related that one appeared, as if it were, the image, as seen in a mirror, of the other. When solutions of these crystals were examined, one set was found to rotate to the right, the other to an equal degree to the left. The dextrorotatory salt yielded ordinary tartaric

acid; the corresponding lævorotatory acid was a hitherto unknown modification: the two together, in equal proportions, constituted racemic acid.

In 1863 Wislicenus published a remarkable memoir on the synthesis of lactic acid. The acid in sour milk was discovered by Scheele in 1785. In 1807 Berzelius discovered a similar acid, called *sarcolactic acid*, in muscle juice; this was erroneously pronounced by Liebig to be identical with that of sour milk. Other forms of lactic acid were made known, the structural character of which was not to be explained by current hypotheses. Wislicenus concluded that their differences could be due only to different arrangements of their atoms in space.

In 1874 the conception of atomic grouping received a remarkable development by the publication of two memoirs—one by Van 't Hoff, and the other by Le Bel—which served to connect molecular structure with optical activity. Confining their attention to carbon compounds, they inferred that all optically active substances contained at least one multivalent atom, united to other atoms or groups, so as to form in space an unsymmetrical arrangement. Van 't Hoff regarded the carbon atom as occupying the centre of a tetrahedron, to the summits of which its valencies were directed. If different groupings are attached to these summits, the structure is *asymmetrical*, and is optically active. The two forms of lactic acid, for example, may be represented by the following space formulæ:—





JACOBUS HENRICUS VAN 'T HOFF.

It will be seen from an inspection of the figures that the one is the image-form of the other, and, no matter how they are turned, they are not superposable; they are right- and left-handed, or, as it is termed, enantiomorphs.

There is no fundamental distinction between the hypothesis of Van 't Hoff and Le Bel as to the effect of asymmetry on optical behaviour. Le Bel regards the effect of asymmetry simply as a necessary consequence of the presence of four dissimilar groupings, and as independent of valency and the geometrical form of the molecule.

It was surmised by Pasteur that every liquid or solid in solution showing optical activity, if crystallisable, would be found to manifest hemihedral faces; but this has not been generally established. Further, it does not always happen that an optically active substance in solution is so when solid. Lastly, optical activity may be latent even in asymmetric carbon compounds if dextro- or lævo- modifications are present in equal proportions, as in racemic acid. Such compounds are, in fact, termed "racemic," or *racemoids*; and they may be separated occasionally by crystallisation, as in Pasteur's method with the tartrates; or as shown by him by the action of the racemoid upon another optically active substance; or, lastly, by taking advantage of the specific action (specific assimilation) of organisms—Pasteur's so-called biochemical method.

It is a physiological fact of great interest that the behaviour of enantiomorphs towards the animal organism is frequently markedly different. Lævo-tartaric acid administered to guinea-pigs is found to be twice as poisonous as the dextro-acid; dextro-asparagine possesses a sweet taste, but lævo-asparagine

is tasteless ; lævo-nicotine is more poisonous than the dextro-alkaloid.

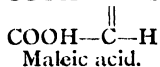
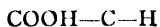
The ferments known as *enzymes* are also found to possess the power of selection, behaving differently towards the different optically active modifications of the same substance. It is frequently observed that an optically active substance may be rendered inactive by the conversion of half the substance into its enantiomorph. This operation was first performed by Pasteur, and may be brought about by heating the substance, either alone or with water, under pressure. Indeed, it is occasionally observed to take place at the ordinary temperature (*autoracemisation*).

By the action of various reagents the derivatives of an optically active substance are found not unfrequently to change the direction of their optical activity. Indeed, by such means one enantiomorph may be changed into another. Thus *lævo*-menthol may be converted into the *dextro* modification by treatment with sulphuric acid.

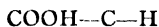
The rotatory power of a substance is frequently modified by the character of its solvent, and varies with the temperature and concentration of the solution. Landolt and Ouglemans found that the specific rotation of dilute solutions of tartrates and of salts of the active alkaloids was independent of the nature of the base and acid respectively present—a fact which finds its explanation in the theory of electrolytic dissociation. It has been known for some years past that the specific rotation of solutions of certain sugars changes with time, being sometimes less and sometimes more than the initial amount. This phenomenon is now known as *multirotation*, or *mutarotation*. It seems to be connected with an alteration in the configuration of the molecules.



There is a special case of stereoisomerism, differing from that of optical isomerism and of structural isomerism (with which we have hitherto been alone concerned), which was predicted by Van 't Hoff in his remarkable work *La Chimie dans l'Espace*, published in 1877—noteworthy as being the first serious attempt to grapple with the problem of spatial molecular grouping, foreshadowed by Wollaston, Berzelius, and, indeed, all the early philosophic thinkers who accepted the atomic theory. The special form of stereoisomerism now referred to, which has been more particularly investigated by Wislicenus, is distinguished as *geometrical isomerism*; not, perhaps, a sufficiently descriptive term, since, comprehensively, all forms of isomerism are really cases of geometrical isomerism. Instances of it are to be met with among the isomeric acids existing as glycerides in certain fats, in cinnamic acid, in stilbene and its derivatives, etc. It was first observed in *maleic* and *fumaric acids*—isomeric acids of the empirical formula  $C_2H_2(COOH)_2$ , obtained by the distillation of malic acid, the characteristic acid met with in the apple and other fruits and in certain other vegetal products. These acids may be represented by the following space formulæ:—



Maleic acid.



Fumaric acid.

which show no asymmetry, and hence no possibility of optical activity or enantiomorphous modifications.

In the case of maleic acid it will be seen that the same groups (COOH or H) are represented on the same side of the molecule—in other words, they are placed symmetrically in a plane—whereas in fumaric

acid, they are placed diagonally or are axially symmetrical. Isomers of the first case are classified as *malenoid* or *cis*-forms, while those of the latter are termed *fumaroid* or *trans*-forms.

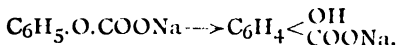
Substances of the character referred to are, as a rule, mutually convertible with more or less ease; they are susceptible of what is called *geometrical inversion*. Thus fumaric acid may be readily converted into maleic acid by heating; maleic chloride is gradually transformed into fumaric chloride at ordinary temperatures. Sunlight, or a particular solvent, or the presence of some substance which acts as a catalyst, may effect the inversion. *Cis* and *trans* isomerism is also met with among cyclic compounds; it occurs among the terpenes; and certain alkaloids, as, for example, cocaine, exhibit it.

Although the doctrine of stereochemistry was first enunciated in the case of carbon, and was, indeed, for a time solely confined to compounds in which carbon was the nucleal element, there is no *à priori* reason why the phenomenon should be so restricted. Van 't Hoff, in fact, in 1878, discussed the question in relation to nitrogen compounds. Stereoisomeric nitrogen derivatives were first obtained by Victor Meyer and his pupils, and the stereochemistry of nitrogen has since proved to be a very fruitful field of investigation, notably in the hands of Goldschmidt, Beckmann, Hantzsch and Werner, Le Bel, Ladenburg, Bamberger, Kipping, H. O. Jones, Pope, and others. The stereochemistry of nitrogen differs from that of carbon, inasmuch as variation of valency plays a far more important part in the case of nitrogen than it has hitherto been observed to do in that of carbon; the spatial representation of the trivalent nitrogen atom differs from that

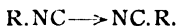
of the pentavalent atom. Le Bel, in 1891, succeeded in obtaining an optically active nitrogen enantiomorph by the application of Pasteur's biochemical method. Optically active compounds have since been prepared by Pope and Peachey and H. O. Jones. Pope and Peachey have also prepared optically active compounds of sulphur, selenium, and tin ; and Kipping has obtained an asymmetric compound of silicon.

In 1863 Geuther, and, independently, Frankland and Duppa, made known the existence of *aceto-acetic ester*. By Geuther this compound was termed *ethyl-di-acetic acid*— $\text{CH}_3\text{C}(\text{OH})\text{:CHCOOC}_2\text{H}_5$ ; by Frankland and Duppa it was considered to be *acetone-carboxylic acid*— $\text{CH}_3\text{CO}\cdot\text{CH}_2\text{COOC}_2\text{H}_5$ . The essential difference in these formulæ, as the two names respectively indicate, is that the first implies that the ester has an acidic or hydroxylic character, proved by its forming characteristic salts ; the other that it contains the group  $\text{CO}$ , proved by its yielding acetone and the usual reactions of the ketones. The attempt to settle the constitution of this substance gave rise to much controversy, and, as it was found to be very reactive, led to a great amount of conflicting experimental work. The ultimate result was to show that both formulæ are correct : at the time of reaction the ester is sometimes hydroxylic, at other times ketonic, or, adopting the terminology of Brühl, it sometimes shows the *enol* form, at other times the *keto* form. Other substances were subsequently found to behave in the same way. In 1885 the question was discussed by Laar, who suggested the term *tautomerism* (ταυτό, the same : μέρος, a part) to denote the fact that one and the same substance could have structural formulæ varying with conditions of reaction and depending upon the migrations

of certain of its atoms within the molecule. During the last twenty years a large number of examples of the kind have been discovered. They are found to occur, not only among aliphatic substances, but in cyclic and heterocyclic compounds. We now know that such intermolecular changes may occur by the migration of any of the elements or groups present in the molecule. Thus, to confine ourselves to simple and well-known examples, the transformation of sodium phenyl carbonate into sodium salicylate, discovered by Kolbe, is due to the wandering of an atom of hydrogen from the benzene residue to oxygen, thus:—



The conversion of the nitriles into the cyanides by heating is due to the transference of the alkyl radical from the nitrogen atom to the carbon—



Alkyl groups may also be transferred from oxygen to nitrogen; a radical may detach itself from a carbon atom and wander to a nitrogen atom; radicals in cyclic compounds may be transferred from the side chains to the nucleus, etc. . . .

The phenomenon, in fact, is now so general that grave doubts have been thrown upon the uniform value of deducing the structural formula of a substance from the study of its decomposition products, or from the nature of its derivatives, owing to the readiness with which tautomerism may occur. The change may be brought about by variation of temperature, by the reagent itself, by the action of a solvent, or the presence of a catalyst—that is, of a substance which *apparently* plays no part in the metamorphosis. Hence the value

of specific reagents as clues to constitution is considerably weakened, since the results may be equivocal. Fortunately, the great extension, within recent years, of the application of physical methods has considerably strengthened our means of gaining an insight into molecular structure; and the investigations of Brühl on refraction and dispersion, of Perkin on magnetic rotation, of Hantzsch on electrical conductivity, of Lowry on solubility, of Lowry and E. F. Armstrong on optical activity, of Knorr and Findlay on melting-points, and, lastly, of Hartley, Dobbie, Lauder, Baly, and Desch on absorption spectra, have collectively afforded valuable information on the mechanism of isomeric change based upon dynamical considerations.

Space will not permit of a more extended treatment of the subject of stereo-chemistry; and certain matters relating to it, as, for example, the phenomena classed under the term *steric hindrance*, must be left unnoticed. This term has reference to the hindrance which certain groups, or the particular distribution in space of certain atoms, exert on the progress or extent of a reaction, as, for example, of hydrolysis or esterification, etc. The influence of special groupings in retarding chemical change is apparently well established, but no comprehensive theory of the subject is yet possible. Until such a theory is forthcoming a dynamical theory of stereo-chemistry is incomplete.

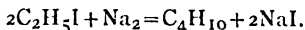
## CHAPTER X.

### ORGANIC SYNTHESIS: CONDENSATION: THE SYNTHESIS OF VITAL PRODUCTS

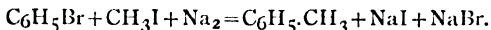
IN its widest sense, the term "synthesis," as used in organic chemistry, means the building-up of carbon compounds, either from their constituent elements or from groups of differently constituted molecules. At one period this term was confined to cases in which the organic compound was prepared from inorganic materials, or from combinations which themselves could be formed from their elements; but latterly it has lost, in large measure, this restricted signification. At the same time, the attempt has been made to indicate by special terms certain classes of synthetical reactions. Thus the special case of the formation of an organic compound by the union of two or, it may be, more molecular groupings is now frequently spoken of as *condensation*.

Organic chemistry has been largely developed by the discovery, from time to time of special reagents and special types of reactions which have shown themselves to be capable of extensive application. Such, for example, was Frankland's discovery, in 1852, of zinc-ethyl—the first of the organo-metallic compounds and the type of a series of substances of great theoretical importance, and of great practical value by reason of their reactive powers. They led to the synthesis of the paraffins, the secondary and tertiary

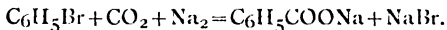
alcohols, and ketones. A few years later Wurtz introduced the use of metallic sodium as a condensing agent, and showed thereby how the hydrocarbon *butane* could be produced from ethyl iodide :—



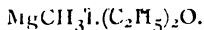
Use was made of the same agent by Fittig, in 1863, in effecting the synthesis of the homologues of benzene by the action of an alkyl iodide upon bromobenzene :—



In like manner Kekule, in 1866, obtained benzoic acid by the action of carbon dioxide upon bromobenzene :—



The readiness with which magnesium can now be obtained, mainly as the result of Sonstadt's efforts to develop its metallurgy, has led to its application, at the suggestion of Barbier, in 1899, in place of zinc. The particular form of magnesium compound now employed as a reagent was prepared by Grignard, in 1900, and is known by his name. It is obtained by bringing an ethereal solution of an alkyl iodide or bromide into contact with magnesium, when the metal is dissolved, forming, in the case of methyl iodide, ,

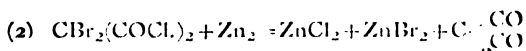
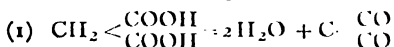


Grignard's reagent has shown itself to be extraordinarily reactive, and a great number of condensations—of hydrocarbons, alcohols, aldehydes, acids, ketones, amides, and additive compounds—have been effected by means of it.

Other condensing reagents of value are aceto-acetic ester, sodium amalgam, sodamide, sodium ethoxide, dimethyl sulphate, zinc chloride, aluminium chloride, fused caustic potash, hydrogen chloride, phenyl-

hydrazine, hydrogen peroxide in presence of a ferrous salt (Fenton's reagent), ammonia, and various amines. The application of these reagents has led to the discovery of a variety of new compounds, the mode of origin of which has served to elucidate their constitution.

The great majority of organic syntheses, especially when they start by the use of inorganic materials, consist in passing from simple to complex molecular groupings by condensation processes. An interesting example of the reverse process is seen in the production of *carbon suboxide*, or *carbon carbonyl*,  $C_3O_2$ , obtained from various malonyl compounds, but most conveniently prepared by the action of phosphoric oxide on malonic acid under diminished pressure, or by treating an ethereal solution of dibromomalonyl chloride with zinc :—

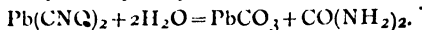


Carbon suboxide is a colourless, extremely mobile, refractive, poisonous liquid, of sp. gr. 1.11, with a strong and peculiar smell. It boils at  $7^\circ$ , and freezes at  $-107^\circ$ . It is stable only at low temperatures; at ordinary temperatures it polymerises to a red solid, which dissolves in water, forming a solution of the colour of eosin. The change is almost instantaneous at  $100^\circ$ . Carbon suboxide is inflammable, burning with a blue but smoky flame:  $C_3O_2 + 2O_2 = 3CO_2$ . Its low boiling point and the high value of its molecular refraction and dispersion, its general resemblance to the metallic carbonyls and ketones, etc., indicate that this remarkable oxide of carbon is, in all probability, the anhydride of malonic acid. Indeed, by the action of water upon it, it is converted into malonic acid.

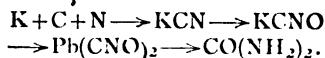


In point of principle, and viewed as chemical operations, the synthesis of vital products is in nowise different from the synthesis of any other group of organic compounds; and the special interest, and even astonishment, at one time created by the artificial preparation of such products have largely died away. The synthetical production of some of the substances formerly known only to be formed by vital action, either in the animal or the plant, has already been incidentally referred to. But it may be convenient to treat the subject of the artificial production of this group of bodies rather more comprehensively and as a sub-section of this chapter on organic synthesis, since their formation by such means constitutes a phase in the development of chemistry, and has undoubtedly exercised a profound influence on scientific thought, and on philosophical and even theological doctrine. During the past fifty or sixty years the chemist has been enabled to form the active principles or characteristic products of many plants and animals. He has built up substances which were formerly regarded as capable of being made only by the very process of living. He has prepared compounds which were at one time considered as only producible by changes in organised matter after death.

Since the date of Wöhler's epoch-making discovery, already referred to (Vol. I., p. 128), *urea* has been synthetically prepared by many reactions, notably by Regnault and Natanson by the action of ammonia on carbonyl chloride, and by Basarow and Dexter from ammonium carbamate. Both these substances can be formed directly or indirectly from their elements. It may also be obtained by the hydrolysis of lead cyanate:—



The successive steps in its production from inorganic materials by this method are :—



Associated with urea as products of metabolism are *uric acid*, *xanthine*, and *sarcine*. Urea was first artificially transformed into uric acid by Horbaczewski, and its synthesis was effected by Behrend and Roosen. Closely related in chemical composition to these substances are *theobromine* and *caffeine*, the characteristic principles respectively of cocoa (the fruit of *theobroma cacao*) ; and of coffee, tea, maté (the leaves of *ilex paraguayensis*) ; “guarana,” obtained from the seeds of the South American plant *paullinia sorbilis*, and the kola-nut of Central Africa. Strecker, in 1860, showed how theobromine may be converted into caffeine ; and Emil Fischer, by similar means, transformed xanthine into theobromine. Since that time xanthine itself has been prepared artificially. Caffeine can now be built up from its elements by a series of transformations effected by a succession of chemists, as follows :—

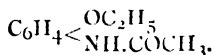
1. Carbon and oxygen give carbonic oxide.—*Priestley, Cruickshank.*
2. Carbonic oxide and chlorine give carbonyl chloride.—*J. Davy.*
3. Carbonyl chloride and ammonia give urea.—*Natanson.*
4. Urea gives uric acid. *Horbaczewski; Behrend and Roosen.*
5. Uric acid gives xanthine.—*E. Fischer.*
6. Xanthine gives theobromine.—*Strecker.*
7. Theobromine gives caffeine.—*E. Fischer.*

Synthetic theobromine is now made on the large scale, and introduced as a soda compound, in combination with sodium acetate, into medicine as a diuretic under

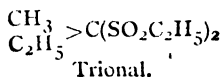
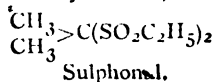
the name of agurin. Synthetic caffeine is also prepared on a manufacturing scale from uric acid through the medium of the methylxanthines. The close relationship of xanthine to uric acid is of great physiological significance, since there is little doubt that the xanthine bases are the most important sources of uric acid within the organism.

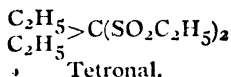
In this connection reference may be made to the large number of synthetic organic products which have been introduced into medicine during the past few years. The investigation of the constitution of the alkaloids has served to show in many cases to what particular molecular grouping the physiological action of the drug is mainly due, and this has led to the production of substances containing these groups, but not necessarily existing as natural products. Among these may be mentioned *antipyrin*, a derivative of the pyrazol group, discovered by Knorr in 1883, and of which upwards of 17,000 kilos, of the approximate value of £35,000, were produced in 1899. This substance is a *phenyl-dimethyl-pyrazolone*.

*Acetanilide*  $C_6H_5NH.COCH_3$ , an aniline derivative, was discovered by Gerhardt in 1853. *Phenacetin* is a derivative of *para*-aminophenol:—

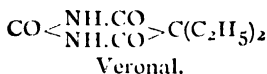


An extraordinary number of synthetical soporifics have been introduced at various times during recent years—*e.g.*, *chloral hydrate*, *veronal*, *sulphonal*, *trional* and *tetronal*, etc. The three last-named substances are closely related, as the following formulæ indicate:—





Sulphonal is prepared by the oxidation of a substance obtained by the combination of acetone and ethyl-mercaptan. *Veronal* is an ethyl compound of barbituric acid, obtained by the condensation of urea and diethyl malonyl chloride :—



Attempts have been made to connect the physiological working of local anæsthetics with particular constitutional groupings, as, for example, in cocaine; and these have led to the introduction of such substances as the *orthoforms*, *nirvanine*, *stovaine*, *alyhine*, *novocaine*, and *adrenaline* into medicine. Adrenaline, used in conjunction with cocaine, has proved itself a most valuable agent in producing what is called *lumbal anæsthesia*, whereby large sections of the lower half of the body may be rendered completely insensitive to pain.

The study of the putrefactive changes of albuminous substances of animal origin, induced by the activity of micro-organisms, has revealed the existence of a number of basic nitrogenous compounds, some of which are highly poisonous. These were classed by Selmi under the generic name of *ptomaines* (πτῶμα, a corpse). Brieger found that the typhoid bacillus yielded a poisonous substance—*typhotoxine*, and that the bacillus of tetanus forms a highly toxic basic body, *tetanine*. All the ptomaines, however, are not poisonous. Some of them, like *choline* (χολή, bile)—originally discovered by Strecker, in bile, in the brain, in yolk of

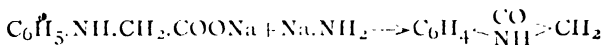
egg, and now found to be among the products of the putrefaction of meat and fish—have been known for some time past. Choline was first synthetically prepared by Wurtz. *Neurine* (νεῦρον, nerve), a derivative of brain substance, is related to choline, and is readily transformed into it, but differs from it in being very poisonous. It has been synthesised by Hofmann and by Baeyer. Another of the so-called corpse-alkaloids—*cadaverine*—has been synthetically formed by Ladenburg. Schmiedeberg and Kopp isolated the poisonous principle of the fungus *agaricus muscarius*, which they named *muscarine*. It occurs with choline, from which it can be readily obtained, among the products of the putrefaction of flesh, as well as in many fungi.

The synthesis of the alkaloids *conine*, *atropine*, *cocaine*, *piperine*, and *nicotine* has been already referred to (p. 105), as also that of *vanillin*, the aromatic principle of the dried fermented pods of certain orchids; *coumarin*, the odoriferous principle of woodruff and of the tonka bean; of *salicylic acid*, *oil of wintergreen*, *oil of mustard*, *bitter-almond oil*, and *camphor*. *Acetic*, *succinic*, *tartaric*, and *citric acids* have also been artificially obtained, and may, indeed, be built up from their elements.

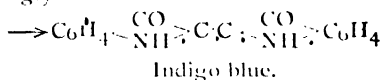
No synthesis of recent years created more widespread interest than that of *alizarin*, first effected by Graebe and Liebermann in 1868. Its successful commercial manufacture by Sir William Perkin in this country and by Caro in Germany created nothing less than a revolution in one of our leading industries, and completely destroyed a staple trade of France, Holland, Italy, and Turkey. To procure alizarin, anthraquinone is treated with sulphuric acid, and the product is fused with alkali and potassium chlorate.

The remarkable industrial results attending the synthetical formation of this madder-product naturally led to attempts to procure other important vegetable dye-stuffs artificially, notably *indigo*. The synthetical production of indigo has been accomplished by the joint labours of many chemists, notably Baeyer, Heumann, and Heymann, and the substance is now prepared on an industrial scale. The starting-point is *naphthalene*, obtained from coal-tar. This is converted into *phthalic acid*, which is then transformed into *phthalimide*. The last-named substance is converted into *anthranilic acid*, which, on treatment with monochloroacetic acid, is changed into *phenylglycin-ortho-carbonic acid*. On melting this with caustic potash it yields *indoxyl acid*, which is transformed into *indoxyl*, and thence into *indigo*.

Another method is to treat the sodium salt of phenylglycin with sodamide, whereby *indoxyl* is at once obtained, and this by condensation yields *indigo blue* :- -



Sodium salt of phenylglycin.      Sodamide.      Indoxyl.



Phenylglycin is obtained by the action of monochloroacetic acid on aniline, which in its turn is obtained through nitrobenzene from benzene. Since benzene can be synthetically prepared by the condensation of acetylene, which can be obtained by the direct union of carbon and hydrogen at a high temperature, it is theoretically possible to build up indigo blue from inorganic materials.

Synthetical indigo blue was placed on the market in 1897 with an almost immediate effect on the production and price of the natural variety, and to-day the output of Bengal indigo has fallen by more than fifty per cent. In 1902 the amount of the natural product was probably not greater than three million kilos, whereas in the same year the production of synthetic indigo was upwards of five million kilos. Before the introduction of the artificial variety the price of pure indigo blue ranged from sixteen to twenty shillings per kilo; by the end of 1905 it had fallen to seven or eight shillings. Mention should be made also of *thio-indigo red* and the *thionaphthene* derivatives, some of which promise to be important colouring matters. In recent years the so-called *sulphur colouring matters* have acquired considerable importance. Space will not permit of any fuller treatment of the development of the manufacture of the artificial organic colouring matters. This industry had its beginnings in England, but it is now mainly carried on in Germany. Its importance may be gleaned from the fact that the value of the production at the present time amounts to not less than £12,500,000 per annum, two-thirds of the output being exported. It demands the services of battalions of skilled chemists, and gives employment to many thousands of artisans.

Some of the most notable achievements of modern synthetical chemistry are to be found in the work of Emil Fischer on the *sugars* and the *proteins*. Although the sugars have from the earliest times been reckoned among the most characteristic products of plant life, and have long been used as food and as sources of alcohol, comparatively little was known until lately of their real nature and mutual relations, in spite of

numerous attempts to elucidate their constitution. Much of the mystery surrounding their chemical history has now been dispelled. Not only has the molecular structure of the more important naturally occurring sugars been unravelled, but a large number of hitherto unknown members of the various groups of the great family to which they belong have been prepared. The first insight into the constitution of these bodies may be said to date from the researches of Kiliani, made about a quarter of a century ago. In 1887 Fischer effected the synthesis of a form of fructose (fruit sugar), and immediately afterwards of ordinary dextro-glucose (grape sugar) and its enantiomorph laevo-glucose, and the two optically active forms of natural fruit sugar. Since that time such sugars as arabinose, xylose, fucose, mannose, sorbose, cane-sugar, maltose, lactose, etc., and the sugars existing as glucosides, have been examined, their stereo-chemical relations defined, and synthetic methods of production devised. Incidentally, their behaviour towards enzymes has been studied, and the remarkable selective action of these ferments on the various groups, due apparently to differences of configuration, has been established, with the result that much light has been thrown on the mechanism of enzyme action and on the general theory of fermentation.

The study of the proteins by Fischer constitutes a new chapter in bio-chemistry. Although long recognised as among the most important of vital products, from the circumstance that they enter into the composition of animal tissues and secretions and are essential constituents of protoplasm, the proteins are among the worst defined substances known to the chemist. They are difficult to separate, as they closely resemble one





EMIL FISCHER.

another, and afford no certain indications of individuality. Very few of them have been obtained in a form in which their identity could be established. *Oxy-hæmoglobin* was isolated some years ago, but the proteins of serum albumin and of egg albumin have only recently been obtained in definite crystalline shape. All the proteins—even the simplest of them—are of great complexity, and possess apparently very high molecular weights. *Hæmoglobin*, for example, appears to have approximately the formula  $C_{158}H_{123}N_{105}O_{218}FeS_3$ , with a minimum molecular weight of 16,600. Indeed, there is experimental evidence to show that it is even considerably higher than this.

The main clues to the nature of these substances have been gained by the systematic study of their hydrolysis, induced by reagents, or by the action of enzymes, whereby they are found to break down into proteoses, peptones, and a great variety of amino acids, some of which have been synthesised. Among the proteins of simplest constitution are the *protamines*, found in the spermatozoa of fish. They are basic substances, especially rich in nitrogen, forming salts with platinum chloride and certain metallic oxides. The best investigated member of the group is *salmine*, obtained from the testicle of the salmon. The products of its hydrolysis have been fairly well ascertained, and their quantitative relation is such that the substance must have at least a molecular weight of 2,045, corresponding to the formula  $C_{81}H_{155}N_{45}O_{18}$ . Many of the albumins and globulins—coagulable proteins contained in the animal tissues—have been isolated in a more or less definite form, and some of them have been found to yield substances akin to carbohydrates. *Thyreoglobulin*, the globulin of the thyroid gland, has been

found to contain iodine, apparently as a normal constituent of a body which can be isolated as a definite proximate principle. The presence of this element is possibly connected with the curative value of the globulin in crétinism. A considerable amount of work on the vegetable albumins has also been done of late years; and some of them, as *edestin* from hemp seed and *zein* from maize, have been obtained in definite form.

The limits of this work preclude a more detailed account of one of the most interesting, but at the same time one of the most obscure, departments of chemistry. The field has hitherto been tilled in a somewhat intermittent and partial manner. Now that it has been entered by chemists of experience and resourcefulness armed with modern methods of cultivation, it will doubtless soon yield a rich harvest of facts, valuable alike to the physiologist and the physician.

There can be no reasonable doubt that the chemical processes of organic life are essentially similar to those of the laboratory. The doctrine that a special "vital force" is concerned in the production of vital products receives no support from the teaching of modern science and is, indeed, contradicted by it. At the same time it must be admitted that we know very little as yet of the real agencies at work in the elaboration and mutations of chemical products in the living organism. Because we have effected the putting together of such a product by purely laboratory processes—it may be indeed, by a variety of different and dissimilar processes—it by no means follows that any one of them is identical with that actually occurring in nature. The building up of materials in the plant by the agency of light, for example, has not yet been imitated in the

laboratory. Many plant products are produced by the action of unorganised ferments—so-called enzymes—none of which the chemist has succeeded in creating.

Processes akin to condensation undoubtedly occur in the living organism; but the means by which they are effected are, in all probability, very different from anything known to the chemist at present. Many laboratory condensations are only accomplished at relatively high temperatures or under considerable pressure—or, in other words, under totally different conditions from those which obtain in the organism.

## CHAPTER XI.

### ON THE DEVELOPMENT OF PHYSICAL CHEMISTRY SINCE 1850

CHEMISTRY and physics are each complementary to the other: that region of inquiry in which they mutually overlap is known as *physical chemistry*. Its beginnings are practically contemporaneous with those of chemistry itself. Its main development has occurred, however, during the last twenty-five years. Certain of its leading features have been referred to already in connection with the establishment of the fundamental principles of chemistry, the explanation of the so-called gaseous laws, the constitution of gases, the relations of their volumes to heat and pressure, and the conditions affecting their transition to the liquid state.

As regards the molecular volumes of gases it has been shown that simple relations are obtained when quantities represented by their respective molecular weights are compared under identical conditions of temperature and pressure—that is, under circumstances in which equal numbers of molecules form the basis of comparison. The investigation of the molecular volumes of liquids is complicated by the uncertainty as to what constitutes in their case a valid condition of comparison. Kopp's assumption that a comparable condition was the temperature at which the vapour pressures of the liquids are equal to the mean atmospheric pressure was justified by the fact that the boiling points of liquids are approximately

two-thirds of their respective critical temperatures. His conclusions have been confirmed and extended by Lossen, Thorpe, and Schiff. It has been shown that the molecular volume of a liquid—that is, the product of its relative density at the boiling-point into its molecular weight—is in the main an additive function modified by constitutive influences. Definite values have thus been obtained for a number of the elements from a comparison of homologous or similarly constituted compounds; and in certain cases these are found to be practically identical with the values of the elements in the uncombined state.

Considerable light has been gained during the last two decades concerning the nature of solution. In its most comprehensive sense *solution* means the homogeneous mixture of two or more substances: thus the gases which exert no chemical action on each other are mutually soluble; gases, liquids, and solids may be soluble in liquids; and, lastly, solids may be soluble in solids, forming what are known as *solid solutions*. The mutual solubility of gases was studied by Dalton, who enunciated the *law of partial pressures*, which states that the total pressure of a mixture of gases is the sum of the pressures exerted by the individual components. This, like all the so-called gaseous laws, is necessarily not strictly accurate under ordinary conditions, but approximates to truth in proportion as the gases are rarefied. Van't Hoff pointed out that the true partial pressures of the components of a gaseous mixture might be experimentally ascertained by the use of a membrane capable of effecting their separation, and on this principle Ramsay measured the partial pressures of a mixture of hydrogen and nitrogen contained in a palladium vessel connected with a manometer. The palladium, at a sufficiently high tempera-

ture, is permeable to hydrogen to the exclusion of the nitrogen. The conditions affecting the solubility of gases in liquids were experimentally studied by Dalton and Henry, and what is known as Henry's law implies that the volume of a gas dissolved by a definite volume of a liquid is independent of the pressure; or, in other words, the density (concentration) of the gas in solution is proportional to that in the space above the liquid. Gases are dissolved by liquids in very different amounts, but nothing definite is known as yet concerning the relation between the nature of the gas and its solubility, although certain broad generalisations are possible. Thus neutral gases—*e.g.*, hydrogen and nitrogen—are sparingly soluble, whereas gases which show acidic or basic properties, such as the hydrogen halides, etc., ammonia, etc., are freely soluble. Easily liquefiable gases are also comparatively soluble as noted by Graham.

Comparatively little is known definitely concerning the conditions of solubility of liquids in liquids. Some liquids are wholly, others partially miscible; and temperature and pressure appear to affect the proportions in which the components form a homogeneous mixture. As regards the solubility of solids in liquids, our knowledge is more extensive, and a considerable body of literature exists on the subject, chiefly concerning solubility of solids in water. The solubility of a solid depends on the temperature of the solvent, and, as a rule, increases with the temperature until a certain amount of the solid has been dissolved, when the solution is said to be *saturated*. If the clear saturated solution be slowly cooled, say, to a particular temperature, it is frequently observed that more of the solid remains in solution than is normal to that temperature; such a solution is said to be *super-*

*saturated*. On adding some of the solid to the supersaturated solution the excess of the *solute* is precipitated. In certain cases of solubility of substances in water, increase of temperature appears to diminish the amount dissolved. In nearly all such cases the difference in solubility is due to differences in the hydration of the solute. The phenomena of solid solutions have been less perfectly investigated, but the facts appear to show that such solutions in general tend to obey the laws regulating the solution of liquids in liquids. Alloys may be looked upon as solid solutions; and Roberts-Austen has shown that metals are capable of intra-diffusion, like liquids and gases respectively.

The general question of solution was greatly developed in 1885 by Van 't Hoff, by specially considering the case of dilute solutions. The gaseous laws are capable of their simplest expression when the gases are rarefied to such an extent that their molecules exert no sensible mutual influence. The case of dilute solutions is analogous. If the solute is present only in very small amount, the mutual influence of its molecules is practically negligible. Under such conditions it obeys the laws hitherto supposed to be applicable only to matter in the gaseous state. •

It may be desirable to explain how this fundamental fact was recognised. It has long been known to the physiologist that certain membranes are *semi-permeable*—that is, they allow of the passage of certain liquids, and of substances in solution, to the exclusion of others. This phenomenon is termed *osmosis*, and is of great biological significance. It was first studied by plant-physiologists, notably by Traube and Pfeffer. Many such semi-permeable membranes can be formed artificially, but the most generally convenient is found to



be one consisting of copper ferrocyanide deposited on the walls of a porous vessel.

If a vessel so prepared be filled with a solution of sugar, and be then placed in water, the water is found to pass through the membrane, but the membrane is impermeable to the sugar. In consequence pressure, termed *osmotic pressure*, is found to occur within the pot, and may be measured by suitable means. These osmotic pressures may at times be very large: thus a 1 per cent. solution of sugar may exert a pressure of half an atmosphere, and in the case of a solution of potassium nitrate of the same concentration it may amount to a couple of atmospheres.

Pfeffer determined the relation of the osmotic pressures to the concentration of solutions of these substances, measuring the pressures in centimetres of mercury by a manometer attached to the closed porous vessel. His results in the case of sugar were as follows:—

<i>Percentage strength (C).</i>	<i>Pressure in cm. of mercury (P).</i>	<i>P/C.</i>
1	53.5	53.5
2	101.6	50.8
4	208.2	52.1
6	307.5	51.3

It will be seen from these numbers that the ratio  $P/C$  is practically constant—that is, *the osmotic pressure varies directly as the concentration*. It was further found that the osmotic pressure exerted by a solution of uniform strength increases with the temperature.

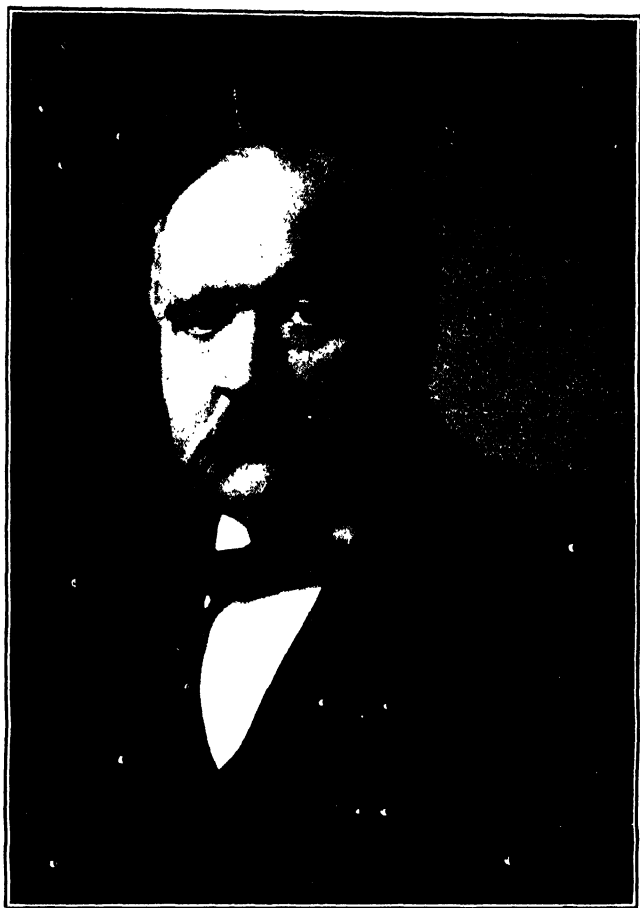
The importance of these observations in relation to the general theory of solution was first recognised by Van 't Hoff. Osmotic pressure was regarded by him as analogous to gaseous pressure. Since  $P/C$  is constant for any one substance, and since for a definite weight of the solute the concentration is inversely as the

volume of the solution, we obtain an equation analogous to the statement of Boyle's law,  $PV = \text{constant}$ . Van 't Hoff also found that the *osmotic pressure is proportional to the absolute temperature*, like the gaseous pressure. From these results, in conjunction with Avogadro's hypothesis, it follows that *the osmotic pressure exerted by any substance in solution is the same as it would exert if present as gas in the same volume as that occupied by the solution, provided that the solution is so dilute that the volume occupied by the solute is negligible in comparison with that occupied by the solvent*. Another important consequence is that *solutes, when present in the ratio of their molecular weights in equal volumes of the same solvent, exert the same osmotic pressure*. Such solutions are said to be *isomotic* or *isotonic*. It can be proved by thermodynamical reasoning that depression of the vapour pressure and freezing-point of a solution is proportional to its osmotic pressure. The significance of this relation in connection with the determination of the molecular weight of a soluble substance has already been referred to (see p. 60).

Determinations of molecular freezing-point depressions by Raoult and others showed that certain substances exerted only about half the osmotic pressure calculated from their known formulæ, whereas others have abnormally high osmotic pressures. The explanation of the discrepancies in the latter case was given in 1887 by Arrhenius, who pointed out that *only those solutions which have abnormally high osmotic pressures are electrically conductive*. This pregnant observation proved to be very fruitful in suggestiveness; and the connection between conductivity and Van 't Hoff's theory of solution was developed by Arrhenius into the doctrine of *electrolytic dissociation or ionisation*—one of the most

important consequences of Faraday's electrolytic laws, the work of Hittorf, and the kinetic conceptions of Williamson and Clausius to which the last quarter of a century has given rise. Arrhenius showed that not only were free ions present in an electrically conductive solution before electrolysis, as maintained by Clausius, but that the proportion of molecules dissociated into ions could be calculated from measurements of electrical conductivity, as well as from measurements of osmotic pressure. Both methods give concordant results—a strong confirmation of the validity of the theory. In a solution of common salt, containing a gramme equivalent of that substance in a litre, Arrhenius calculated that only about three-tenths of the salt exists as  $\text{NaCl}$ , the remaining seven-tenths being resolved into independent ions of chlorine (chloridion) and sodium (sodion):  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$ , each moving freely in all directions, like gaseous molecules. On passing the current, electrodes placed in the solution exert a directive action on the free ions, these being alone concerned in determining the conductivity, the un-ionised molecules or the solvent itself exercising no influence. Methods of determining the migration velocity of the ions have been worked out by Hittorf, Kohlrausch, Lodge, and others.

The theory of ionisation affords a satisfactory explanation of many chemical phenomena. It accounts for the characteristic properties of acids, and explains why different acids have varying "strengths" and why a "weak" acid has the same "strength" as the "strong" acid at high equivalent dilutions: in each case the acid is nearly completely ionised—in other words, the "strength" of an acid depends on the concentration of its hydrogen ions. So, too, the "strength" of a base is related to



SVANTE AUGUST ARRHENIUS.

the number of its hydroxyl ions. Aqueous ammonia is relatively a "weak" base—its solution contains few hydroxyl ions. On the other hand, caustic potash is a "strong" base—its solution, on moderate dilution, is almost completely ionised:  $\text{KOH} = \text{K}^{\cdot} + \text{OH}'$ , the positive ion being represented by one or more dots, and the negative ion by one or more dashes. The theory accounts, too, for many phenomena in analytical chemistry—such as why magnesia is precipitated by ammonia only in the absence of ammonium chloride, and why sulphuretted hydrogen throws down zinc sulphide in the absence of hydrochloric acid. It also serves to explain many thermo-chemical facts observed by Hess, Thomsen, and others, such as the fact that the heat of neutralisation of the "strong" acids and bases is independent of their nature, and has the uniform value of 13,700 calories, in agreement with the value, as calculated by Van 't Hoff, for the reaction  $\text{H}^{\cdot} + \text{OH}' = \text{H}_2\text{O}$ , deduced from Kohlrausch's measurements of the conductivity of water at varying temperatures.

Certain phenomena relative to the effect of concentration (mass action) in determining chemical change—many of which have been studied by Ostwald and his pupils, as, for example, why two "dilute" solutions can be mixed together without thermal disturbance; numerous hydrolytic actions; the alkalinity and acidity of salts on solution; the behaviour of the "indicators" in analysis; such phenomena as the precipitability of common salt in aqueous solution by hydrogen chloride; the influence of an excess of a precipitant; the varying behaviour of reagents; the varying colour of salt solutions; the reason why water is formed in so many reactions; why a potential difference occurs at the surface of two electrolytic solutions, etc.—phenomena for the

most part otherwise unintelligible, are all capable of explanation by means of it.

Although, in the above statement, we have been mainly concerned with aqueous solutions, it should be said that the theory of ionisation is applicable to other solvents, organic and inorganic. Moreover, it should be added, the theory has not been universally accepted as accounting for all the phenomena of solution. Many substances form definite hydrates which can be isolated, and it is a moot point whether such hydrates are capable of existing in aqueous solution, as contended by Mendeléeff, Pickering, Kahlenberg, Armstrong, and others. Such hydrates are, however, unstable compounds, affected by temperature changes, and dissociable on dilution in accordance with the law of concentration (mass action). Further, there is evidence, largely based on the work of Kohlrausch, H. C. Jones, and Lowry, to show that the ions in aqueous solutions of electrolytes are themselves hydrated.

Limitations of space preclude further attempts to deal with the development of physical chemistry during the last half-century, and many important matters must remain practically unnoticed.

The subject of thermo-chemistry is mainly the creation of the last half-century, elaborated by the labours of Hess, Andrews, Thomsen, Favre and Silbermann, and Berthelot. The work of Wenzel and Berthollet on the influence of molecular concentration on chemical change has been greatly extended by Berthelot, Guldberg and Waage, Julius Thomsen, Van 't Hoff, Harcourt and Esson, and Le Chatelier; and the theory of mass action and the nature of reversible processes are now capable of definite expression, and can be proved independently by thermodynamical and kinetic reasoning. The

phenomena of catalysis and the action of enzymes and of fermentation in general have received attention from many investigators. The phenomena of gaseous transpiration have been studied by Graham, Maxwell, and O.E. Meyer. Thermal dissociation has been experimentally observed by Deville, Troost, and others, and mathematically investigated by Willard Gibbs and Van der Waals; and its analogy to electrolytic dissociation has been established. The nature of gaseous explosions has been investigated by Berthelot, Le Chatelier, Abel, and Dixon. Important work has been done by Gladstone, Lorentz, Landolt, Nasini, Brühl, and others, on the connection between the nature and constitution of substances and their optical characters. Similar work has been done by Sir William Perkin as regards their magnetic rotation, and by Thorpe and Rodger with reference to their viscosity. The theory of phases, originating with Gibbs and developed by Van der Waals and Roozeboom, has been greatly extended. Sir J. J. Thomson and Sir J. Larmor have elaborated an electrical theory of the atom. Barlow and Pope have traced the relation between valency and volume, and the accurate measurements of Groth and of Tutton have extended our knowledge of the crystallographic relations of correlated substances.

Lastly, the whole subject of photo-chemistry, although originating with the observations of Ingenhousz, Scheele, and Senebier, may be said to have been studied only within our own time, notably by Bunsen and Roscoe, Fringsheim, Pfeffer, Vogel, and Abney.

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